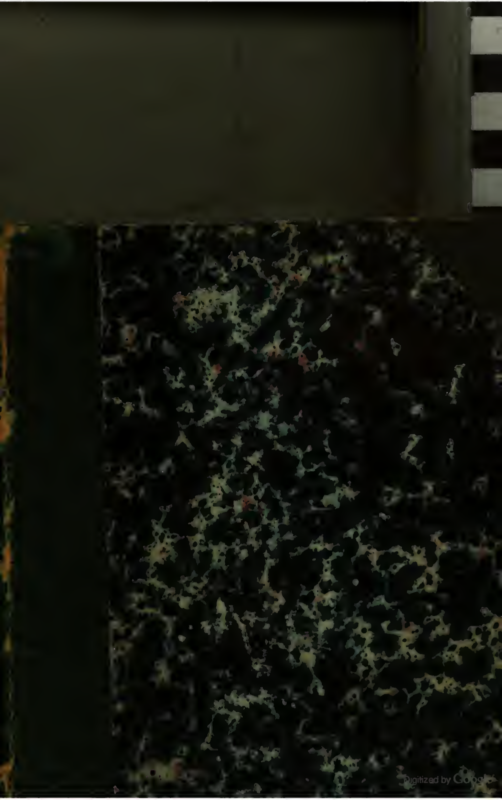

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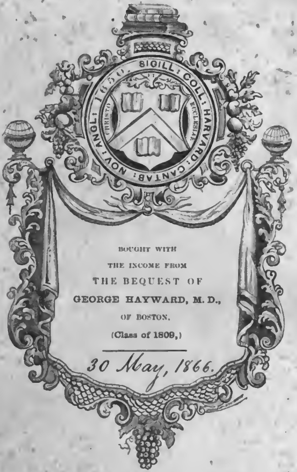
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# A
# DICTIONARY OF CHEMISTRY.

VOL. IV.

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# A DICTIONARY

OF

# CHEMISTRY

AND THE

ALLIED BRANCHES OF OTHER SCIENCES.

BY

HENRY WATTS, B.A., F.C.S.

EDITOR OF
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.

*IN FIVE VOLUMES.*

VOL. IV.

NACRITE—PYRUVIC ACID.

LONDON:
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1866.

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⁂ Articles communicated by the several contributors are signed with their initials; articles taken from URE's *Dictionary of Chemistry* (fourth edition, 1831) are signed with the letter U; those which have no signature are by the Editor.

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# DICTIONARY OF CHEMISTRY.

## N.

**NACRITE.** A mineral from Brunswick in the State of Maine, consisting of white pearly scales, having the feel of a soft earthy talc, and containing, according to Thomson (*Outlines of Mineralogy*, i. 244), 64·44 per cent. silica, 28·84 alumina, 4·43 ferric oxide, and 1·0 water (= 98·71). *Talcite*, from Wicklow in Ireland, is similar in physical character, but of different chemical composition, containing only about 45 per cent. of silica. A mineral also called *nacrite* from the mica-slate of the Alps, in which Vanqnelin found 50 per cent. silica, 26 alumina, 5 ferric oxide, 1·5 lime and 17·5 potash, appears to have been a mica.

**NAGYAGITE.** *Foliated Tellurium, Black Tellurium, Tellurium-glance, Blattertellur, Blättererz.*—Native telluride of lead and gold, occurring sometimes in dimetric crystals, oP . 2 P∞ . P, in which the length of the principal axis is 1·298; cleavage basal; more frequently however in lamellar masses; sometimes granular. Hardness = 1—1·5. Specific gravity, 6·85—7·2. Opaque, with metallic lustre and blackish lead-grey colour; streak the same. Thin laminæ very flexible. When heated in a tube, it gives off sulphurous anhydride, and yields a white sublimate consisting chiefly of tellurous anhydride. Melts easily before the blowpipe, burning with a blue flame, and forming on the charcoal a yellow deposit which disappears in the inner flame, and finally leaving a button of malleable gold.

Nagyagite contains, according to the most recent analysis by Schönlein (Ann. Ch. Pharm. lxxxvi. 201), 9·70 per cent. sulphur, 30·09 tellurium, 50·95 lead, 9·10 gold, 0·53 silver, and 0·99 copper, agreeing with the formula $(Ppb; Au^2).(Te; S)$. Specimens analysed by Berthier and Folbert (*Rammelsberg's Mineralchemie*, p. 57) were found to contain antimony (3·77—4·55 per cent.).

Nagyagite occurs in veins at Nagysg and Offenbanya in Transylvania, associated at the former place with sylvanite, silicate of manganese, blende and gold, and at the latter with antimony ores. It is also said to occur abundantly at Whitehall, near Fredericksburgh in Virginia. (*Kenngott's Uebersicht*, 1850–51, p. 143.)

**NANCEIC ACID.** Braconnot's name for the acid which he found in the wash-liquor of the preparation of wheat-starch, &c., afterwards shown to be lactic acid (iii. 453).

**NAPHTHA.** A term applied by the older chemical writers to a variety of volatile, mobile, strong smelling, inflammable liquids, chiefly belonging to the class of ethers; thus the sulphate, nitrate and acetate of ethyl were called *Naphtha vitrioli, N. nitri, N. aceti*, &c. Subsequently it was restricted to the liquid hydrocarbons, which issue from the earth in certain localities, and appear to be produced by the action of a moderate heat on coals or bitumens. More recently it has been again extended so as to include most of the inflammable liquids produced by the dry distillation of organic substances. The liquids thus designated are:—

1. **Boghead** or **Bathgate Naphtha,** also called *Photogen* and *Paraffin oil.*—This liquid was originally obtained by distilling the Torbane hill mineral or Boghead coal at as low a temperature as possible; but it is now known that any cannel coal or even bituminous shale, if subjected to similar treatment, will yield the same products.

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The crude distillate is a mixture of several liquid hydrocarbons, together with acid and basic compounds. When purified by redistillation and subsequent treatment with sulphuric acid and caustic soda, it yields an oil consisting of a mixture of various fluid hydrocarbons holding paraffin in solution. By distillation with water, it is separated into a volatile liquid (*a*) lighter than water and containing little or no paraffin, and a less volatile liquid which contains paraffin, and after further purification by successive treatment with oil of vitriol and chalk, is well adapted for lubricating machinery. When heated to between −1° and +4·5° C. (30° and 40° F.), it deposits a portion of the paraffin, the remaining liquid being a saturated solution of paraffin in the fluid hydrocarbons.

The volatile oil (*a*) is a mixture of a great number of hydrocarbons, belonging to three different series, viz., the olefines, $C^nH^{2n}$; the benzene series, $C^nH^{2n-6}$; and the marsh-gas series or alcoholic hydrides, $C^nH^{2n+2}$. To separate these bodies it is necessary first to subject the liquid to a long series of fractional distillations, whereby it is resolved into portions boiling at intervals of 10°, and then to treat each fraction, first with bromine to remove the olefines, and then with strong nitric acid which removes benzene and its homologues. The hydrocarbons remaining after these successive treatments consist of the alcoholic hydrides, $C^nH^{2n+2}$. The following have been separated:—hydride of hexyl, $C^6H^{14}$, boiling at 68°; hydride of octyl, $C^8H^{18}$, boiling at 119°; hydride of decatyl, $C^{10}H^{22}$, boiling at 159°; and hydride of dodecatyl, boiling at 202°.

**Bone Naphtha,** *Bone oil*, *Dippel's animal oil*, already described (i. 625), consists chiefly of a mixture of hydrocarbons which have not yet been investigated with certain volatile bases, viz. ammonia, pyrrhol ($C^4H^5N$), and bases of the series $C^nH^{2n+3}N$ and $C^nH^{2n-5}N$, homologous with ethylamine and pyridine respectively, together with smaller quantities of acids.

3. **Caoutchouc Naphtha** or *Caoutchoucin* (i. 736), is for the most part a mixture of polymeric hydrocarbons, chiefly caoutchin and isoprene.

4. **Coal Naphtha** is obtained by the distillation of coal-tar (see i. 1038). The "light oil" after separation from the heavier "creosote oil," or "dead oil," is rectified, whereby a further portion of heavy oil is separated and crude coal-naphtha is obtained. This is agitated with sulphuric acid to free it from organic bases, and the supernatant liquid, after further rectification, yields the "highly rectified naphtha" or "benzole" of commerce, which is chiefly a mixture of five oily hydrocarbons of the benzene series, viz. benzene, $C^6H^6$, boiling at 80·4°; toluene $C^7H^8$, at 114°; xylene, $C^7H^{10}$, at 126°; cumene, $C^9H^{12}$, at 144°; and cymene, $C^{10}H^{14}$, at 177·5.° The liquid hydrocarbons of coal-naphtha boiling at higher temperatures have not been much studied. Ordinary coal-naphtha likewise contains traces of olefines.

The *basic* constituents of crude coal-naphtha, which are removed by agitating the liquid with sulphuric acid, may be obtained in the free state by distilling the acid liquid with excess of alkali, and separated from one another, partly by fractional distillation, partly by fractional crystallisation of their platinum-salts. These bases belong to two series, the one series consisting of pyridine and its homologues, represented by the general formula $C^nH^{2n-5}N$, viz. pyridine, $C^5H^5N$; picoline and its isomer, aniline, $C^6H^7N$; lutidine, $C^7H^9N$; and collidine, $C^8H^{11}N$; while the other series of bases, $C^nH^{2n-11}N$, is isomeric with chinoline, $C^9H^7N$, and its homologues, viz. leucoline, $C^9H^7N$; iridoline, $C^{10}H^9N$; and cryptidine, $C^{11}H^{11}N$ (see LEUCOLINE, iii. 583).

The alcohol-bases, $C^nH^{2n+3}N$ (methylamine and its homologues), which occur in bone-oil, appear to be altogether absent from coal-naphtha.

Coal-tar also contains large quantities of naphthalene, $C^{10}H^8$ (p. 4).

The "dead oil" or less volatile portion of coal-tar contains a considerable quantity of phenol, phenylic alcohol, phenic acid, carbolic acid, or coal-tar creosote, $C^6H^6O$, together with several hydrocarbons of high boiling point, and existing at ordinary temperatures as crystalline solids; these have been but imperfectly examined. The last portions of liquid which pass over in the distillation of coal-tar contain two of these solid hydrocarbons, viz. chrysene, $C^6H^4$, and pyrene, $C^{15}H^{12}$, the former being insoluble, the latter soluble in ether (see CHRYSENE, i. 958). The last semifluid portions of the tar also contain anthracene or paranaphthalene, $C^{14}H^{10}$, which separates out in the solid state, when the semifluid oil is exposed to a low temperature (see PARANAPHTHALENE).

5. **Mineral** or **Native Naphtha.** *Petroleum*, *Rock-oil*, *Steinöl.*—This is an inflammable liquid of a more or less tarry consistence, which issues from the earth in various localities, occurring in large quantities in Persia, at Rangoon in the kingdom of Burmah, in Canada, and other parts of North America, and is generally associated with solid bitumen or asphalt, as in the great pitch-lake of Trinidad (i. 426). These naphthas consist almost wholly of mixtures of hydrocarbons; the older analyses made of them are of little value, because the proximate constituents were not separated with

sufficient care; recently, however, the American petroleum has been made the subject of an elaborate investigation by Pelouze and Cahours (Ann. Ch. Pharm. cxxiv. 289; cxxvii. 196; cxxix. 87), who have shown that it is made up almost entirely of the series of alcoholic hydrides, $C^nH^{2n+2}$, from hydride of tetryl, $C^4H^{10}$, upwards, the greater portion however consisting of hydride of hexyl, $C^6H^{14}$ (see Hydrides, iii. 181). Hence, and from the composition of Boghead and cannel coal-naphtha, it would appear that these hydrides, homologous with marsh-gas, constitute the chief products of the decomposition of coal and bituminous substances at comparatively low temperatures (see Petroleum).

*Burmese naphtha* or *Rangoon tar* is obtained by sinking wells about 60 feet deep in the soil, the liquid gradually oozing out and being removed as soon as a sufficient quantity has accumulated. There are about five hundred of these naphtha wells, yielding annually about 412,000 hogsheads. This naphtha contains about 11 per cent. of solid paraffin. De la Rue and Müller (Proc. Roy. Soc. viii. 221), by distilling the crude naphtha in an atmosphere of steam, superheated for the higher temperatures, have resolved it into the following portions:

| | | |
|---|---|---|
| Below 100° C. | Free from paraffin | 11 |
| 110° to 145° | A little paraffin | 10 |
| 145° to melting point of lead | Containing paraffin but still fluid at 0° | 20 |
| At about the melting point of lead | Sufficiently solid to be submitted to pressure | 31 |
| Beyond melting point of lead | Quantity of paraffin diminishes | 21 |
| Last distilled | Pitchy matters | 3 |
| Residue in still | Coke containing a little earthy impurity | 4 |
| | | 100 |

The proportion of hydrocarbons removable from the various distillates by strong sulphuric acid, nitric acid, or a mixture of both acids, is in most cases small, increasing generally however with the boiling point of the liquid, and varying from one-tenth to nearly a third of the compound hydrocarbon; hence it is probable that this naphtha likewise consists, for the most part, of homologues of marsh-gas. The hydrocarbons removed by nitric acid consist of benzene, toluene, xylene, and cumene.

6. **Shale Naphtha.** *Shale oil.*—The naphthas obtained by the dry distillation of the various bituminous shales or schists present great diversity of composition, and but few of them have hitherto been submitted to careful examination. The bituminous shale of Dorsetshire, the naphtha from which has been examined by C. Gr. Williams (Chem. Soc. Qu. J. vii. 97), contains much nitrogen and sulphur, arising to a great extent from the presence of a large quantity of semi-fossilised animal remains. Hence the crude naphtha is intolerably fetid. It may be sweetened and freed from its basic and acid constituents by repeated treatment with sulphuric acid and caustic soda, and then contains nearly the same constituents as Boghead naphtha, viz. benzene and its homologues, various olefines, and small quantities of the homologues of marsh-gas. The basic constituents removed by sulphuric acid consist of pyridine, and its homologues; the acid portion is chiefly phenic or carbolic acid.

The French shale oils have been examined by Laurent and St. Evre, but without any very satisfactory results. Laurent's analyses have been quoted by Gerhardt (*Traité*, iv. 423), to show that the hydrocarbons approach in composition to the formula $nCH^2$ (calc. 85·7 per cent. carbon; anal. 85·6—86·2 per cent.).

Laurent, by subjecting the portion of shale oil boiling between 80° and 150° to the action of boiling concentrated nitric acid, obtained an acid which he called ampelic acid (i. 201), having the composition of salicylic acid, $C^7H^6O^3$, and probably formed by the oxidation of one of the homologues of benzene.

The various bitumens and asphalts, of which immense deposits exist in many countries, yield by distillation oils or naphthas of similar nature to shale oil.

The shale oil prepared at Reutling from "Posidonienschiefer," yields by distillation a small quantity of tar not exceeding 3·5 per cent. The hydrocarbons obtained from it are said to have a composition represented by the formula $C^nH^{2n-4}$, the greater portion, which boils between 160° and 175°, being $C^7H^{12}$. (Harbordt, Ann. Ch. Pharm. cxxiv. 14.)

For further details respecting the preparation, properties, and composition of the several naphthas above mentioned, see the series of excellent articles on Naphthas by C. Gr. Williams in the new edition of *Ure's Dictionary of Arts, Manufactures and Mines*, iii. 220–233.

**NAPHTHADIL.** A substance derived from mineral naphtha; it is black, with a weak greasy lustre; copper-brown in fracture; does not change in the light, melts at the same temperature as wax, and burns with a clear flame. (Dana, ii. 470.)

**NAPHTHALAMIDE.** Syn. with PHTHALAMIDE.

**NAPHTHALASE.** $C^{20}H^7O$?. (Laurent, Ann. Ch. Phys. [2] lix. 326.)—To prepare this compound, nitro-naphthalene is heated with great care with 8 or 10 times its weight of hydrate of barium, the retort being filled up to the neck. Ammonia, naphthalene, and an oil then pass over, while a thicker oil condenses in the neck of the retort, and solidifies on cooling. In order to obtain the naphthalase, the neck of the retort is to be cut off near the bulb, and washed with ether, by which means the oily impurities and any naphthalene present are removed.

Naphthalase is a yellow substance which sublimes without fusing at 250°. At a still higher temperature it melts and boils, giving off a yellow vapour which condenses in small spangles, which are deposited in long yellow needles. It is insoluble in alcohol, almost insoluble in ether, soluble in water. Its most characteristic property is its power of colouring sulphuric acid a beautiful violet tint. The smallest quantity gives the reaction, and the colour is not destroyed in hermetically closed tubes, even after the lapse of two years.

Naphthalase does not appear to be destroyed by nitric acid, inasmuch as after being heated with that acid, it still dissolves in sulphuric acid with a blue colour. Chlorine does not remove from it its power of colouring oil of vitriol.

No success has attended the various efforts which have been made to isolate the coloured substance which naphthalase forms with sulphuric acid, with a view to industrial purposes. C. G. W.

**NAPHTHALENE.** Syn. *Naphthaline, Naphthalin.* $C^{10}H^8$. (Garden, Thomson's Annals of Philosophy, xv. 74; Faraday, Phil. Trans. 1826; Reichenbach, Schw. J. lxi. 175; lxviii. 233; Dumas, Ann. Ch. Phys. l. 182; Dumas and Stas, *ibid.* lxxxvi. 40. Laurent, *ibid.* lxix. 214; Révue Scientif. vi. 76. *Products of its oxidation:* Révue Scientif. xiv. 560. *Chlorinated and brominated derivatives:* Ann. Ch. Phys. xlix. 218; lii. 275; Révue Scientif. xi. 361; xii. 193; xiii. 66, 579; xiv. 74, 313. *Nitric derivatives:* Ann. Ch. Phys. lix. 376; Révue Scientif. xiii. 67. *Sulphuric acid derivatives:* Révue Scientif. xiii. 587.) For an extended list of memoirs on naphthalene, see *Gmelin's Handbook*, xiv. 1.

*History.*—Naphthalene appears to have been first noticed publicly by Garden, who extracted it from the crude distillate from coal. It was also observed by Reichenbach during his researches on destructive distillation. It was first analysed by Faraday, who not only determined its composition accurately, but also arrived at its true atomic weight. The most laborious researches upon naphthalene were made by Laurent, who was more or less engaged in studying it for nearly twenty years. Some of the earliest and most decided instances of substitution of chlorine, &c., for hydrogen were discovered in the course of his studies of this hydrocarbon.

*Formation.*—Generally produced when organic bodies are distilled *per se* at very high temperatures. 1. By distilling coal. When coal-tar is distilled, the naphthalene which it contains is found to accompany the liquids which come over at almost all the temperatures observed. It is, however, more abundant in the portions distilling about 216°. Even the cymene distilling at about 178° is often so contaminated with naphthalene as to be isolated only with the greatest difficulty and great loss. Naphthalene is often retained in a fluid condition in a remarkable manner by the substances which accompany it in the crude coal oil. It not unfrequently happens that a liquid which has remained fluid for months, even in cold weather, may by repeated treatment with sulphuric acid, followed by refrigeration, be almost entirely converted into solid naphthalene. It is also found in the tar of shales and analogous substances accompanying paraffin.—2. Alcohol and ether vapour, and even olefiant gas and acetic acid vapour, yield more or less naphthalene when passed through red-hot tubes.

3. Petroleum and most essential oils passed through red-hot tubes also afford it (Saussure, Berthelot).—4. Camphor vapour passed over red-hot quicklime, yields naphthalene (Frémy). From the above considerations it is not remarkable that naphthalene should be found in soot and lamp-black. Dumas at one time asserted that naphthalene exists ready formed in coal; this, however, has been denied by Reichenbach. Since, however, it is certain that paraffin exists ready formed in Boghead coal and certain cannels, it is to be desired that this question should be determined more carefully.—4. Sulphide of carbon vapour mixed with sulphuretted hydrogen, or a mixture of these two with carbonic anhydride, when passed over spongy copper or iron at a dull red-heat, yields naphthalene and other products (Berthelot). Some chemical substances containing no hydrogen, such as the proto-

chloride of carbon, $C^2Cl^3$, when passed together with hydrogen through a red-hot tube yield naphthalene. (Berthelot.)

*Preparation.*—The quantities of naphthalene which are obtained as bye-products in the preparation of coal-naphtha are so large, that even if a use for it were discovered, it would scarcely be necessary to take special measures for its extraction. It is often found in quantities (amounting in some cases to tons) in the tanks in which pitch-oil (heavy coal-oil) is stored. Coal-tar from which the lighter oils have been removed by a preliminary distillation is distilled in large iron stills. The distillate is received in puncheons, and the process is carried on until the liquid is heavier than water. The first 200 gallons from a charge of 7000, contain but little naphthalene; all the rest of the distillate abounds in it. To extract the naphthalene, small quantities of sulphuric acid may be shaken with the oil, and then after settling for a short time, may be run off. The supernatant oil on coling to 0° deposits large quantities of the naphthalene. On repeating the process more and more will be obtained, until, in many instances, almost the whole will become solid. Previous to cooling it is sometimes advisable to distil the oil after the treatment with acid and removal of the tarry deposit. During the distillation large quantities of sulphurous acid are given off. Where a difficulty is found in getting the naphthalene to deposit, a treatment with a little bleaching powder, after the acid, and then distilling, will generally effect the separation.

*Purification.*—The crude greasy naphthalene obtained as above may be drained on cloth strainers until most of the oil is removed. The remainder may then be got rid of by pressure in strong bags. Exposure to the air for a long time greatly improves the product. The roughly purified substance may then be redistilled, the receiver being changed when the product comes over colourless. To obtain it in large crystals it may be melted in basins on the sand-bath. Covers of paper should be pasted over, and care should be taken that the basins are not more than half full. When the contents are melted and beginning to sublime, the whole may be allowed to cool. When quite cold a large quantity of colourless crystals will be found between the cake of naphthalene and the paper cover. They may be removed with a feather. The residue may be pressed to extract oily impurities, and the process can be repeated until almost the whole has been converted into crystals (Otto). The methods of purification given can be employed on any scale, from the largest to the smallest, without fear of failure; it will be unnecessary therefore to describe other methods.

*Properties.*—Naphthalene when pure consists of brilliant white scaly crystals, very friable, strongly and unpleasantly odorous, and having a density of 1·153 at 18°, and of 0·9778 in a melted state of 79·2°. As obtained by sublimation, the crystals are generally rhombic tables of 122° and 78°, the hexagonal form arising from truncation of the acute angles. According to Laurent, naphthalene may be obtained in monoclinic prisms, by spontaneous evaporation from a solution in ether. According to Chamberlain, it crystallises from turpentine in prisms having pyramidal terminations. It melts at 79·2° (H. Kopp), and boils, according to the last observer, at 218°, the barometer standing at 760 mm. It sublimes even at low temperatures; distils readily along with fluid hydrocarbons, and even along with the vapour of water. On water it rotates somewhat like camphor. Its vapour-density is 4·528 according to Dumas, but as determined by Natanson (in an apparatus enabling the volume of vapour to be measured in a manner analogous to Gay-Lussac's method), the value 4·46 was obtained. Theory for two volumes, requires 4·43. It is insoluble in cold, and almost insoluble in boiling *water*; dissolves readily in *alcohol*, *ether*, *fatty* and *essential* oils and most oils obtained by destructive distillation, whether hydrocarbons or oxidised bodies. It also dissolves in *acetic* and *oxalic acids*. Its solution in *turpentine* is accompanied by a fall in temperature.

*Decompositions.*—1. Naphthalene burns with a dense smoky flame. (The condensed soot of naphthalene forms one of the varieties of commercial lamp-black.) When it is passed over red-hot *lime* or *baryta*, carbonate of calcium or barium is formed and hydrogen is given off.—2. By *chlorine*. Chlorine acts with energy on naphthalene, heat being evolved and hydrochloric acid formed. The mass at first melts, but on continuing the stream of gas it gradually solidifies again. At this stage, the principal products of the reaction are hydrochlorate of chloronaphthalene, $C^{10}H^7Cl.HCl$ (Gerhardt's chloride of naphthalene), and dihydrochlorate of dichloronaphthalene, $C^{10}H^6Cl^2.2HCl$. The continued action of chlorine causes the substitution to go still further. The substitution of chlorine for the hydrogen of naphthalene may be continued until the whole is replaced, and the compound $C^{10}Cl^8$ is reached. The hydrochloric acid produced by union of the hydrogen of the naphthalene with the chlorine is not given off, but remains in combination with the chlorinated derived radicle; it may, however, be removed by treatment with alkalis or by the action of heat; the chlorine which replaces the hydrogen, on the other hand, is unaffected by heat or alkalis.

Laurent's results assume a complicated appearance, owing to the circumstance that substitution-products of the same formula may be obtained in several different ways, and any difference in the mode of preparation causes the resulting bodies, in the majority of instances, to vary in melting point, crystalline form, hardness or other characters; they have been described by him as isomeric modifications, and individualised by characteristic letters. In some of the cases cited by Laurent, there is little doubt that the variations in properties were due to the different specimens not being in an equally high state of purity, but this will certainly not account for all the observed differences.

3. By *bromine*. Bromine acts upon naphthalene, forming numerous compounds according to the manner in which the ingredients are allowed to react on each other. The reaction between the two substances is energetic, hydrobromic acid being liberated and substitution compounds formed. By acting with bromine upon chlorinated naphthalene, substances may be obtained having the same composition as those procurable by treating brominated naphthalene with chlorine. According to Laurent, some of these, although having the same crystalline form, differ according to the order of the formation.

4. *Iodine, phosphorus, sulphur, chloride of carbon, cyanogen,* and *hydrochloric acid,* are without action on naphthalene. An attempt to form the iodide of a more hydrogenated hydrocarbon, by acting with fuming hydriodic acid on naphthalene, gave no result, although the acid had a density of 1·9 and was heated with the naphthalene in a sealed tube to 100° C. (Possibly at a higher temperature the experiment might be more successful.)

5. *Nitric acid* acts upon naphthalene. If moderately strong nitric acid be added to naphthalene and allowed to act at ordinary temperatures, nitro-naphthalene is slowly formed. The nitro-naphthalene so produced may be converted into di-nitro-naphthalene by boiling for a long time with strong nitric acid. The reaction does not take place very readily, but a mixture of nitric acid, Nordhausen sulphuric acid and nitro-naphthalene yields di-nitro-naphthalene readily, if heated to boiling in an apparatus allowing the vapours to become condensed and flow back.

6. An oxidising mixture consisting of *acid chromate* of *potassium* with *sulphuric* or *hydrochloric acids* appears to form two compounds according to the state of concentration, the temperature, or other circumstances. One of these substances is said to have the formula $C^{9}H^{4}O^{4}$, and to be of a beautiful rose colour. It appears to have feeble acid properties. The other is said to contain $C^{10}H^{6}O^{4}$, and to have more decided acid characters. The subject requires re-examination.

7. *Nitrous acid* and *aqua-regia* both appear to yield nitro-naphthalene and an oily body.

8. *Sulphuric acid* forms several conjugated acids with naphthalene; they will be found described under their respective headings.

According to Fritzsche, naphthalene may be made to unite with *picric acid* atom to atom, by dissolving the two substances in hot alcohol or benzene, and cooling.

The limits of this work will not admit of an extended account of the vast number of substances obtained by Laurent and others by acting upon naphthalene with chlorine, bromine, nitric acid and sulphuric acid. We shall, however, endeavour to give, as concisely as possible, a brief statement of the nature and methods of production of the more important derivatives. For a full account, the reader is referred to Gerhardt's *Traité*, iii. p. 413, *et seq.*, and the Cavendish Society's translation of Gmelin's Handbook, xiv. 1, *et seq.* In the first-named work the article on naphthalene occupies 51, and in the second 92 pages.

### *Chlorine-derivatives.*

The table on p. 7 contains a list of the principal chlorides and bromides of naphthalene. They are decomposed by heat and also by alcoholic potash, hydrochloric or hydrobromic acid being removed, and chlorinated or brominated naphthalene produced. The names as given by Gmelin generally accord with Laurent's earlier views.

The following table contains a list of the principal substitution-products derived from naphthalene by the substitution of chlorine or bromine or both for the hydrogen of naphthalene. They are for the most part produced by treating the substances given in the table of chlorides and bromides with alcoholic potash.

*Chloro- and Bromo-naphthalenes.*

| | | | |
|---|---|---|---|
| Chloronaphthalene | $C^{10}H^{7}Cl$ | Tetrachloronaphthalene | $C^{10}H^{4}Cl^{4}$ |
| Bromonaphthalene | $C^{10}H^{7}Br$ | Bromotrichloronaphthalene | $C^{10}H^{4}BrCl^{3}$ |
| Dichloronaphthalene | $C^{10}H^{6}Cl^{2}$ | Dibromodichloronaphthalene | $C^{10}H^{4}Br^{2}Cl^{3}$ |
| Dibromonaphthalene | $C^{10}H^{6}Br^{2}$ | Tetrabromonaphthalene | $C^{10}H^{4}Br^{4}$ |
| Trichloronaphthalene | $C^{10}H^{5}Cl^{3}$ | Dibromotrichloronaphthalene | $C^{10}H^{3}Br^{2}Cl^{3}$ |
| Tribromonaphthalene | $C^{10}H^{5}Br^{3}$ | Hexchloronaphthalene | $C^{10}H^{2}Cl^{6}$ |
| Bromodichloronaphthalene | $C^{10}H^{5}BrCl^{2}$ | Perchloronaphthalene | $C^{10}Cl^{8}$ |

*Chlorides and Bromides of Naphthalene.*

| *Names according to this work.* | *Names according to Gerhardt.* | *Names according to Gmelin.* | *Gerhardt's formulæ.* | *Gmelin's formulæ.* |
|---|---|---|---|---|
| Dichloride of Naphthalene | Chloride of Naphthalene | Hydrochlorate of Chloronaphthalene | $C^{10}H^8.Cl^2$ | $C^{10}H^7Cl.HCl$ |
| Dichloride of Bromonaphthalene | Chloride of Bromonaphthalene | Hydrochlorate of Chlorobromonaphthalene | $C^{10}H^7Br.Cl^2$ | $C^{10}H^6BrCl.HCl$ |
| Dibromide of Tribromonaphthalene | Bromide of Tribromonaphthalene | Hydrobromate of Quadribromonaphthalene | $C^{10}H^5Br^3.Br^2$ | $C^{10}H^4Br^4.HBr$ |
| Tetrachloride of Naphthalene | Bichloride of Naphthalene | Bihydrochlorate of Bichloronaphthalene | $C^{10}H^8.Cl^4$ | $C^{10}H^6Cl^2.2HCl$ |
| Bromotrichloride of Naphthalene | Bichlorobromide of Naphthalene | Bihydrochlorate of Bromochloronaphthalene | $C^{10}H^8.Cl^3Br$ | $C^{10}H^6BrCl.2HCl$ |
| Tetrachloride of Chloronaphthalene | Bichloride of Chloronaphthalene | Bihydrochlorate of Terchloronaphthalene | $C^{10}H^7Cl.Cl^4$ | $C^{10}H^5Cl^3.2HCl$ |
| Tetrachloride of Dichloronaphthalene | Bichloride of Bichloronaphthalene | Bihydrochlorate of Quadrichloronaphthalene | $C^{10}H^6Cl^2.Cl^4$ | $C^{10}H^4Cl^4.2HCl$ |
| Tetrachloride of Dibromonaphthalene | Bichloride of Bibromonapthalene | Bihydrochlorate of Bibromobichloronaphthalene | $C^{10}H^6Br^2.Cl^4$ | $C^{10}H^4Br^2Cl^2.2HCl$ |
| Tetrabromide of Dichloronapthalene | Bibromide of Bichloronaphthalene | Bihydrobromate of Bibromobichloronaphthalene | $C^{10}H^6Cl^2.Br^4$ | $C^{10}H^4Br^2Cl^2.2HBr$ |
| Tetrabromide of Bromochloronaphthalene | Bibromide of Bromochloronapthalene | Bihydrobromate of Terbromochloronaphthalene | $C^{10}H^6BrCl.Br^4$ | $C^{10}H^4Br^3Cl.2HBr$ |
| Tetrabromide of Dibromonaphthalene | Bibromide of Bibromonapthalene | Bihydrobromate of Quadribromonaphthalene | $C^{10}H^6Br^2.Br^4$ | $C^{10}H^4Br^4.2HBr$ |
| Tetrachloride of Dibromochloronaphthalene | Bichloride of Bibromochloronapthalene | Bihydrochlorate of Bibromoterchloronaphthalene | $C^{10}H^5Br^2Cl.\ {}^4$ | $C^{10}H^3Br^2Cl^3.2HCl$ |
| Tetrabromide of Tribromonaphthalene | Bibromide of Tribromonaphthalene | Bihydrobromate of Pentabromonaphthalene | $C^{10}H^5Br^3.Br^4$ | $C^{10}H^3Br^5.2HBr$ |

*Note.* For convenience the term *chlorée* has been rendered *chloro*; thus *naphtaline chlorée* has been rendered *chloronaphthalene*. *Other liberties have also of necessity been taken with the nomenclature, but they are rendered absolutely necessary by the progress of science; for instance, the substances containing four atoms of chlorine &c. outside the radicle or chlorinated radicle termed *bichlorides* by Gerhardt, are rendered *tetrachlorides* in this article. In order also to attain harmony with the nomenclature adopted generally in this dictionary, Greek numerical prefixes have been substituted for the Latin.

We shall consider briefly the mode of preparation of each of the substances enumerated in the above lists.

*Dichloride of Naphthalene.* Gerhardt's *Chloride of Naphthalene*, $C^{10}H^8Cl^2$.—This, the first product of the action of chlorine on naphthalene, may be prepared by passing chlorine over naphthalene until the product has passed through an oily stage and begins to become granular. The operation must not be carried so far as to chlorinate all the naphthalene. The mixture is to be heated in a dish for a long time to a temperature between 50° and 60°, then dissolved in ether and cooled to —10°, and the ethereal solution mixed with alcohol and oil exposed to the air until two-fifths of the oil have been deposited: this oil contains the oily chloride of naphthalene. The third fifth may also be collected; it is the solid chloride, $C^{10}H^8Cl^4$, in a state of purity.

Dichloride of naphthalene is oily, soluble in all proportions in ether, but less soluble in alcohol. On distillation it decomposes slowly, giving off hydrochloric acid, and yielding chloronaphthalene, $C^{10}H^7Cl$. With alcoholic potash it yields the last-named substance and chloride of potassium.

*Dichloride of Bromonaphthalene.* $C^{10}H^7Br.Cl^2$. *Laurent's Subchloride of Bronaphtase.* When chlorine is passed into crude bromonaphthalene, it thickens and deposits a crystalline matter. Ether is poured on the product, and the mixture is allowed to remain for 24 hours. The oily portion is to be decanted, and the crystalline powder washed with ether and then dissolved in a large quantity of boiling ether. By spontaneous evaporation the chloride of bromonapthalene is deposited in small rhomboidal tables resembling those of dichloride of naphthalene. The crystals are derived from an oblique prism with a rhombic base (Gerhardt, *loc. cit.*). Melts at 165°.

*Dibromide of Tribromonaphthalene.* $C^{10}H^5Br^3.Br^2$. *Subbromide of Bronaphtise.* Produced, together with dibromide of dibromonapthalene when dibromonaphthalene is treated with bromine. On boiling the mixture with ether, the dibromide of tribromonaphthalene dissolves, and on spontaneous evaporation is deposited as a flocculent powder consisting of white microscopic needles. It decomposes on distillation, giving off hydrobromic acid, a little bromine, and a crystalline matter very slightly soluble in ether.

*Tetrachloride of Naphthalene.* Gerhardt's *Bichloride of naphthalene.* $C^{10}H^8.Cl^4$. *Hydrochlorate of chloronaphtalese.*—This substance exists in two isomeric modifications.

*Modification α.*—When a rapid current of chlorine is passed over naphthalene in rather large quantity (say one or two pounds) the naphthalene fuses, hydrochloric acid is disengaged, and, if the current be sustained, the whole, after some time, begins to thicken again. The mixture at this point contains oily dichloride of naphthalene, tetrachloride of naphthalene *α*, the modification *β*, and tetrachloride of chloronaphthalene, the last two in small quantity. Ether is to be poured on the mixture to render it more fluid. After repose for some hours the oily portion is to be decanted and the residue thrown on a filter. After being well drained the residue is dissolved in benzene and allowed to cool very slowly. The tetrachloride soon begins to crystallise out, and if the solution be tolerably large in quantity (half a gallon or a gallon) fine rhombohedrons will be deposited. The writer has sometimes obtained them nearly a quarter of an inch on the side. They are colourless, transparent and exactly resemble calc-spar. They also possess powerfully the property of double refraction.

This modification of tetrachloride of naphthalene is inodorous, insoluble in water, slightly soluble in alcohol, moderately so in ether, but very soluble in benzene, rock-oil and analogous liquids. It melts at 160° and solidifies to a crystalline mass on cooling. If a crystal be added to the partially fused chloride, the whole will solidify at about 150° in rhombic tablets. On the other hand, if the chloride be perfectly fused and allowed to cool without addition, the mass sometimes solidifies at 150° in rhombic tables, and sometimes between 100° and 110° in concentric needles.

It is decomposed by distillation, giving off hydrochloric acid and an oily matter. Only a trace of carbon (1 or 2 per cent.), remains in the retort. The distillate consists of a mixture of four isomeric forms of dichloronaphthalene. These products are always accompanied by a small quantity of undecomposed tetrachloride of naphthalene. Alcoholic potash converts it into the two modifications *e* and *ad* of dichloronaphthalene.

*Modification β.*—This variety of tetrachloride of naphthalene is distinguished from *α* by its solubility in ether. It is formed, as already observed, at the same time as the modification *α* when chlorine is passed over naphthalene. It is contained in the oily portion rendered more fluid by ether which has been directed to be poured off from the solid portion which consists chiefly of *α*. The liquid containing ether is

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to be cooled to 0° and kept at that temperature for 48 hours; it will then solidify to a mass resembling frozen olive oil. The solid portion may be collected on linen and freed from the mother-liquid by pressure. The solid is to be dissolved in ether containing about one-tenth of alcohol. The solution left to spontaneous evaporation yields a crystalline mass containing both the modifications. The mass must be well pressed, dissolved in boiling alcohol, and very slowly cooled. The first crystals which form will be almost pure α, the rest of the crops will be successively richer in β. By repeated crystallisations from ether the latter may be obtained pure. Its purity may be known by its dissolving rapidly and without residue in ether.—It is colourless, inodorous, very soluble in ether, alcohol, benzene, and similar hydrocarbons. It crystallises in small lamellæ of indeterminable form which unite into globes often of considerable diameter. Submitted to distillation it gives off hydrochloric acid, an oil, and the modification *c* of dichloronaphthalene. Boiled with alcoholic potash it yields an oil and the modification *f* of dichloronaphthalene.

*Bromotrichloride of Naphthalene*, $C^{10}H^8.Cl^3Br$.—To prepare this substance, tetrachloride of naphthalene (modification β) is treated with bromine in a closed flask for 48 hours; the mixture washed with warm alcohol to remove the excess of bromine and undecomposed tetrachloride; and the crude dichlorobromide of naphthalene purified by crystallisation from boiling ether. It is colourless, more soluble in ether than the modification α of tetrachloride of naphthalene, but less soluble than the variety β. It is decomposed both by distillation and by alcoholic potash.

*Tetrachloride of Chloronaphthalene.* Gerhardt's *Bichloride of chloronaphthalene.* Laurent's *Chloride of chloronaphthase.* $C^{10}H^7Cl.Cl^4$.—This substance may be prepared from the tetrachloride of naphthalene, and like that compound exists in two different modifications, one being solid and the other an oil.

*Solid modification.*—According to Gerhardt, this is the most remarkable of all the naphthalic chlorides for the size and beauty of its crystals. It may be prepared by acting with chlorine upon tetrachloride of naphthalene, but the process is very difficult. A more advantageous plan is to heat the crude dichloride with chlorine gas. This is the fluid portion which has been directed to be rendered more liquid by ether in order to separate it more readily from the solid tetrachloride of naphthalene in the process for the preparation of the modification α of that substance (p. 8). The ether is expelled by heat, and chlorine passed through the oil for two or three days. If the fluid becomes too thick to allow of the passage of the gas, it must be gently warmed. A little ether is then added to render the whole more fluid, and it is left at rest in a cool place. A crystalline deposit is then formed perfectly resembling the modification α of tetrachloride of naphthalene (Gerhardt's bichloride of naphthalene, $C^{10}H^8.Cl^4$). The oily portion is removed by decantation, and the deposit thrown on a filter and washed with a little ether to remove the oily portion which adheres to it. The solid is then dissolved in boiling ether and put aside for several days in a flask with a wide mouth merely closed with a piece of paper. The crystals which form are sometimes a mixture of modification α of tetrachloride of naphthalene and the tetrachloride of chloronaphthalene. The crystals of the latter are easy to recognise by their size; they must be picked out with forceps and redissolved in the ethereal mother-liquid. They may be rendered perfectly pure by one or two recrystallisations from ether.

*Properties.*—Colourless, transparent, inodorous, insoluble in water, little soluble in alcohol, pretty soluble in ether, more so than the modification α of tetrachloride of naphthalene. Melts at 105°, and the liquid may be cooled to 54° without solidifying; it then slowly assumes the form of nodules formed of concentric zones; the last portions remain viscid until they fall to the ordinary temperature. But if after heating to 105° or 110° a small fragment of a crystal be added, the liquid crystallises rapidly at 105°, forming fine oblique tables with a rhombic base.

It is entirely decomposed by distillation, hydrochloric acid being disengaged, and the two modifications *a* and *d* of terchloronaphthalene formed.—Boiling nitric acid converts it into chloroxynaphthalic, phthalic, and oxalic acids, with other products.

*Liquid modification.*—This compound is the oily substance which has been directed to be removed by decantation from the solid modification above described. Distillation converts it almost entirely into the *a* modification of trichlororonaphthalene mixed with a small quantity of an oily matter.—Alcoholic potash produces the same results.

*Tetrachloride of Dichloronaphthalene*, $C^{10}H^6Cl^2.Cl^4$. Laurent's *Perchloronaphthalese.*—This substance exists in three modifications, *c*, *a*, and *x*; they are produced from the corresponding modifications of dichloronaphthalene.

*Modification c.* To prepare this substance, the modification *c* of dichloronaphthalene is kept in fusion and treated with chlorine; no hydrochloric acid is evolved. The product is to be washed with ether, dissolved in boiling ether, and crystallised. It is colourless, inodorous, not very soluble in ether, and less so in alcohol; melts at 141°.

The crystals obtained by spontaneous evaporation of an ethereal solution form brilliant oblique rhombic prisms. It is decomposed by distillation, yielding hydrochloric acid and the *b* modification of tetrachloronaphthalene mixed with a small portion of the *a* modification of the same substance. Alcoholic potash gives rise to the *k* modification.

*Modification a.* An oily liquid obtained by treating dichloronaphthalene *a* with chlorine. Distillation and the action of a boiling solution of alcoholic potash equally give rise to tetrachloronaphthalene *a*.

*Modification x.* An oily liquid produced by treating dichloronaphthalene *x* with chlorine. Distillation converts it into tetrachloronaphthalene *c*. Alcoholic potash gives a similar product.

*Tetrachloride of Dibromonaphthalene*, $C^{10}H^6Br^2.Cl^4$. Laurent's *Chloride of Bronaphthese.* When chlorine is passed into fused dibromonaphthalene, a very thick oil is formed, which on dilution with ether deposits the substance sought in the form of a crystalline powder. It is colourless, only slightly soluble in alcohol or ether. Melts at about 155°, and on solidifying crystallises in prisms. On distillation it gives off bromine, a hydracid, bromotrichloronaphthalene β, and tetrachloronaphthalene α.—Alcoholic potash transforms it into a substance crystallising in needles and soluble in ether.

*Tetrabromide of Dichloronaphthalene*, $C^{10}H^6Cl^2.Br^4$. Laurent's *Bromide of Chloronaphthase.*—Prepared by the action of bromine on an excess of dichloronaphthalene *c*. Colourless, very slightly soluble in ether. Melts a little above 100°, turning red and evolving bromine. When it is heated until no more bromine be evolved, the modification *c* of dichloronaphthalene is regenerated.

*Tetrabromide of Bromochloronaphthalene*, $C^{10}H^6BrCl.Br^4$. Laurent's *Bromide of Chlorobronaphthase.* Prepared by treating chloronaphthalene with bromine. An active effervescence ensues, due to the disengagement of hydrobromic acid. If the bromine is in excess, crystals of the tetrabromide are formed on repose. It is purified by solution in a large excess of boiling ether. On cooling it is deposited in very small lustrous prisms. Before melting it becomes red and gives off bromine and hydrobromic acid. An oil remains behind which, like trichloronaphthalene, solidifies on cooling in rectangular figures crossed by two diagonals bristling with needles parallel to each other.

*Tetrabromide of Dibromonaphthalene*, $C^{10}H^6Br^2.Br^4$.—Gerhardt's *Bibromide of Bibromonaphthalene.*—Prepared by pouring bromine over naphthalene or dibromonaphthalene. It is usually deposited after a few hours as a white crystalline powder which may be purified by washing with ether. It is but slightly soluble in boiling ether, from which however it is deposited on cooling in microscopic rhombic tables. By distillation it yields hydrobromic acid, bromine, and tetrabromonaphthalene, which condenses in the neck of the retort.—It is decomposed with difficulty by boiling alcoholic potash.

*Tetrachloride of Dibromochloronaphthalene*, $C^{10}H^5Br^2Cl.Cl^4$.—Produced by the action of chlorine on tetrachloride of dibromonaphthalene. Melts at 150°, and on cooling crystallises in rhomboïdal tables. If heated a little above its melting point, it remains soft and transparent on cooling, and only partially solidifies, forming an opaque mass without any crystalline appearance; if then gently heated, it crystallises in rhombic tablets. It is only sparingly soluble in ether.

It decomposes on distillation, yielding bromine, a hydracid, and three other substances, namely Laurent's bromochloronaphthalene B, a chloride or chlorobromide fusible at 100°, and a small quantity of a substance which crystallises in small opaque needles.—A boiling solution of alcoholic potash converts it into the α modification of dibromotrichloronaphthalene, $C^{10}H^5Br^2Cl^3$.

*Tetrabromide of Tribromonaphthalene*, $C^{10}H^5Br^3.Br^4$.—To prepare it, dibromonaphthalene is to be heated with bromine, and the action finished in sunshine. It may be purified by crystallisation from ether. It is but slightly soluble in ether. Its other properties do not appear to have been studied. By distillation it yields bromine and a substance not yet examined.

### *Chloro- and Bromonaphthalenes.*

*Chloronaphthalene*, $C^{10}H^7Cl$. *Laurent's Chloronaphthalase.*—Prepared by boiling dichloride of naphthalene with alcoholic potash. On adding water to the product of the reaction, an oil separates which may be purified by distillation. It may also be prepared, but not advantageously, by distilling dichloride of naphthalene.

It is oily, colourless, soluble in all proportions in ether; distils without change; is not attacked by potash.

Decomposed by bromine with effervescence, yielding hydrobromic acid and tetrabromide of bromochloronaphthalene, $C^{10}H^{6}BrCl.Br^{4}$. Chlorine converts it into a peculiar oil which yields the *a* modification of trichloronaphthalene when treated with potash. Chlorine with aid of heat converts chloronaphthalene into tri- or tetrachloronaphthalene.

*Bromonaphthalene*, $C^{10}H^{7}Br$.—Prepared by the action of bromine on naphthalene, avoiding excess, which would cause the formation of dibromonaphthalene. It is a colourless oil which distils without alteration. Unaltered by an alcoholic solution of potash. Chlorine combines with it, yielding dichloride of bromonaphthalene, $C^{10}H^{7}Br.Cl^{2}$. Bromine converts it into dibromonaphthalene and other brominated products.

*Dichloronaphthalene*, $C^{10}H^{6}Cl^{2}$.—This substance exists, according to Laurent, in seven different modifications, namely *a*, *c*, *ad*, *e*, *f*, *x*, and *y*. [The letters adopted as distinctive marks by Laurent have reference to certain properties which the substances bearing them have in common; thus the bodies marked *a* are always soft; the only one marked *b* happens to be brittle (*cassant*); those marked *c* are always in needles of 113° or thereabouts; those marked *e* are in needles of 94°, and so on. The reason for the adoption of these special letters does not seem to have been made public.] The modifications *a*, *c*, *f*, and *x*, are obtained by distilling the alpha modification of tetrachloride of naphthalene; *ad* and *e* by treating the tetrachloride with potash; and another *y* by submitting dinitronaphthalene to the action of chlorine.

The following table exhibits the principal properties of these substances.

*Distinctive Characters of the Dichloronaphthalenes.*

| | *a.* | *c.* | *ad.* | *e.* | *f.* | *x.* | *y.* |
|---|---|---|---|---|---|---|---|
| FORM. | Liquid. | Needles 112° 30′. | Needles 122°. | Needles 94°. | Tables 103°. | Liquid. | Sublimed laminæ. |
| MELTING-POINT. | | 50° | 28° to 30° | 31° | 101° | | 95° |
| PRODUCT with CHLORINE. | Oily tetrachloride of dichloronaphthalene which is converted by potash into tetrachloronaphthalene *a*. | Solid tetrachloride of dichloronaphthalene. | Dichloronaphthalene *ac*. | | Laminæ of chlonaphtone. | Liquid tetrachloride of dichloronaphthalene, which is converted by potash into tetrachloronaphthalene *c*. | |
| PRODUCT with BROMINE. | | Tetrabromide of dichloronaphthalene | Bromodichloronaphthalene *a*. | | Dichlorodibromonaphthalene *b*. | A liquid. | |

*Dibromonaphthalene*, $C^{10}H^{6}Br^{2}$.—Prepared by the action of bromine on naphthalene or bromonaphthalene; it may be purified by crystallisation from alcohol. Long needles, inodorous, very soluble in alcohol and in ether. Melts at 59°, and crystallises on cooling into a fibrous mass. It is volatile without decomposition, and is not attacked by potash. Bromine acts on it, giving rise to several compounds.—Fuming sulphuric acid forms dibromosulphonaphthalic acid.

*Trichloronaphthalene*, $C^{10}H^{5}Cl^{3}$.—According to Laurent, there are no fewer than *seven* isomeric modifications of this substance. It will be quite unnecessary to do more than quote the table on page 12, giving their principal properties.

*Tribromonaphthalene*, $C^{20}H^{5}Br^{3}$.—Obtained by heating an excess of bromine with dibromonaphthalene. Fine yellow needles. Melts at 60°, and sometimes does not solidify until cooled to the temperature of the air.

*Bromodichloronaphthalene*, $C^{20}H^{5}BrCl^{2}$.—Several grammes of the modification *ad* of dichloronaphthalene are to be mixed in a flask imperfectly closed, with a slight excess of bromine. Hydrobromic acid is evolved, which, with the excess of bromine, may be removed by washing with a few drops of alcohol and a little ammonia. The residue is to be dissolved in boiling alcohol. On cooling, the bromodichloronaphthalene deposits in fine needles. The unattacked dichloronaphthalene remains in the alcoholic solution.

This substance is colourless, tolerably soluble in alcohol, very soluble in ether; and of the consistence of wax. Crystallises by spontaneous evaporation of its ethereal solution

*Distinctive characters of the seven varieties of Trichloronaphthalene.*

| | *a.* | *ac.* | *c.* | *g.* | *d.* | *ad.* | *ae.* |
|---|---|---|---|---|---|---|---|
| **FORM.** | Six-sided prisms of 120°. | Six-sided prisms, rhombus of 113°. | Long needles, rhombus of 113°. | Prisms terminated by needles, rhombus of 130°. | Like *g* rhombus of 124°. | Silky needles, rhombus of 122°. | Needles of which the section is a hexagon derived from a rhombus of 122°. |
| **HARDNESS.** | Soft. | Soft. | Elastic, brittle. | Unelastic, brittle. | Like *g*. | | Soft. |
| **MELTING-POINT.** | 75° | 66° | 78° to 80° | 69° to 70° | 88° to 90° | 160° | 93° |
| **STATA after FUSION.** | Soft rectangular parallelograms. | Same as *a*. | Transparent rosettes becoming slowly opaque by repose. | Transparent rosattes becoming suddenly opaque on contact with a foreign substance. | Needles moiré transparent becoming opaque on repose. | Transparent rosettes becoming opaque on repose. | Soft rectangular parallelograms becoming harder after e time. |
| **ETHER.** | Extremely soluble. | Very soluble. | Soluble. | Soluble. | Soluble. | Slightly soluble. | Less soluble than *a*. |
| **ALCOHOL.** | Very slightly soluble. | Soluble. | Soluble. | Soluble. | Soluble. | Slightly soluble. | More soluble than e. |

in six-sided needles with angles between 120° and 121°. Melts about 80°. Distils without decomposition.

*Tetrachloronaphthalene*, $C^{10}H^{4}Cl^{4}$, exists in four different modifications.

*Distinctive characters of the Tetrachloronaphthalenes.*

| | *a.* | *b.* | *c.* | *k.* |
|---|---|---|---|---|
| **ELASTICITY.** | Soft. | Brittle. | Flexible. | Flexible. |
| **FORM.** | Six-sided prisms of 120°. | Oblique prisms with oblique base of 103°, 101°, 100°. | Long needles, rhombus of 94°. | Flat needles, rhombus of 100°. |
| **MELTING-POINT.** | 106° | 125° | 170° | 125°. |
| **CRYSTALLISATION after FUSION.** | Microscopic rosettes. | Needles. | Needles. | Rosettes. |
| **ETHER.** | Very soluble. | Very slightly soluble. | Very slightly soluble. | Very slightly soluble. |
| **NAPHTHA.** | | | Very weak boiling solution becomes filled with long needles. | Very weak solution deposits small needles grouped in masses which only fill a small portion of the liquid. |

*Bromotrichloronaphthalene*, $C^{10}H^{4}BrCl^{3}$, exists in three different modifications, $\alpha$, $\beta$, $\gamma$.

*Modification* $\alpha$ is prepared by the action of bromine on the modification $\alpha$ of trichloronaphthalene. It forms colourless six-sided prisms with angles = 117° 30′, and two = 125°. Soft like wax. After fusion it crystallises in microscopic rosettes between 105° and 106°. Volatile without decomposition.

*Modification β* is prepared by the action of bromine on dichloronaphthalene. It is like the α modification of tetrachloronaphthalene, except that the crystals are better defined. Crystallises in six-sided prisms, with four angles = 120° 30′ and two = 119°. It is of the consistence of wax, and after fusion solidifies at about 100° in microscopic rosettes.

*Modification γ* is prepared by distillation of tetrachloride of dibromonaphthalene, $C^{10}H^6Br^2.Cl^4$. During the operation bromine and the vapours of hydrobromic and hydrochloric acids are disengaged. The receiver contains a mixture of trichloronaphthalene (modification α) and the γ modification of bromotrichloronaphthalene. The first may be removed by solution in ether, a white powder then remaining which on treatment with a large quantity of boiling ether, dissolves, and separates on spontaneous evaporation, in small brilliant prisms.

Oblique prisms with oblique bases, the angles of the sides being 102° 30′, and the inclination of the base to the sides being 101° and 103°. Very slightly soluble in ether and in boiling alcohol. Volatile without decomposition.

*Dibromodichloronaphthalene*, $C^{10}H^4Br^2Cl^2$.—There are, according to Laurent, two isomeric modifications, α and β.

*Modification* α.—Prepared by treating the variety *f* of dichloronaphthalene with bromine. Hydrobromic acid is then disengaged, and in a few minutes the fluid solidifies in needles, which are to be washed with cold ether and dissolved in a very small quantity of hot ether. By slow evaporation the substance is deposited in small but brilliant doubly oblique prisms, having the angles of the faces = 101° 30′ to 102° 50′ and 101° 15′. It melts at 170°, and crystallises on cooling in flat needles.

*Modification* β.—Prepared by treating dibromonaphthalene with chlorine. Doubly oblique prisms, melting at 166° and distilling without alteration. Solidifies on cooling into a fibrous mass. Very slightly soluble in ether or boiling alcohol.

*Tetrabromonaphthalene*, $C^{10}H^4Br^4$, appears to exist in two isomeric modifications. When tetrabromide of dibromonaphthalene is distilled, hydrobromic acid and bromine are disengaged, and a white matter distils, which contains two substances. To separate them, they are first washed with ether and then introduced with more ether into a strong glass tube, which, after being closed at the lamp, is to be heated to 100° in a water-bath. On cooling, the tube is to be opened and the substances removed. One crystallises in short brilliant prisms, and the other in very fine needles. They may easily be separated mechanically.

Tetrabromonaphthalene crystallises in oblique prisms with oblique base, in all respects resembling those of the *b* modification of tetrachloronaphthalene. Soluble in alcohol and ether. They distil without alteration and resist the action of potash. The needles are probably tetrabromonaphthalene *a*; they are elastic, brittle, and very slightly soluble in ether.

*Dibromotrichloronaphthalene*, $C^{10}H^3Br^2Cl^3$.—This substance also exists in two isomeric modifications.

*Modification α* may be prepared by boiling tetrachloride of dibromocloronaphthalene ($C^{10}H^5Br^2Cl.Cl^4$) with alcoholic potash. A white powder is obtained which may be dissolved in a very large quantity of boiling ether or benzene. The crystals can be obtained by spontaneous evaporation. Brilliant prisms belonging to the triclinic system. After fusion it crystallises at 166° in long prisms. Volatile without decomposition. Unacted on by potash.

*Modification β*, prepared by the action of bromine on tetrachloride of naphthalene in sunshine, is a white powder almost insoluble in ether, fusible, and crystallising on cooling in rectangular parallelograms crossed by two diagonals.

*Hexchloronaphthalene*, $C^{10}H^2Cl^6$, is prepared by the prolonged action of chlorine, aided by heat, on the alpha modification of trichloronaphthalene. If the product contains perchloronaphthalene, it may be purified by means of ether, in which the latter substance is comparatively insoluble.

Six-sided prisms with angles of 120°. Of the consistence of wax, and may be bent without difficulty. Dissolves in about 20 times its weight of ether. Scarcely soluble in alcohol, but very soluble in benzene. After fusion it solidifies at 143° in microscopic rosettes. Volatile without decomposition, and, like its congeners, unattacked by potash. Even sulphuric acid dissolves only a very small quantity. It is with difficulty attacked by boiling nitric acid, which however finally transforms it into perchloroxinaphthyl, $C^{10}Cl^6O^2$.

*Perchloronaphthalene*, $C^{10}Cl^8$.—Prepared, like the last substance, by the prolonged action of chlorine on alpha-trichloronaphthalene kept in fusion. The hexchloronaphthalene may be removed by ether and the perchloronaphthalene may be obtained from the residue by boiling it in benzene or petroleum.

Pale yellow needles, or very brittle, four-sided prisms, of which the angles are 112° 30′, and 67° 30′. Very slightly soluble in ether, even on boiling. Volatile without decomposition and unattacked by potash.

In addition to the above chlorine and bromine compounds, Laurent has described a number of substances containing fractional parts of atoms of chlorine, bromine, and hydrogen. Many of these substances appear to be mixtures, but others have resisted all efforts to separate them into bodies having more satisfactory formulæ. It is however observable that the substances may be traced to the parent hydrocarbon by adding the fractional atoms together; thus Laurent's *bromide of bronaphthine* is represented by the formula $C^{10}H^{5.5}Br^{2.5}Br^{4}$. Now since 5·5 + 2·5 = 8, the hydrogen is all accounted for, and the substance would appear to be tetrabromide of naphthalene, in which 2·5 atoms of hydrogen are replaced by 2·5 atoms of bromine. It will not be necessary to do more than give the following list of substances described by Laurent containing fractional formulæ. The names are those of Laurent.

| | |
|---|---|
| Bronaphthine | $C^{10}H^{5.5}Br^{2.5}$ |
| Bromide of bronaphthine | $C^{10}H^{5.5}Br^{2.5}.Br^{4}$ |
| Chloride of chloronaphtane | $C^{10}H^{7.5}Cl^{.5}.Cl^{4}$ |
| Chlorophtone F | $C^{10}H^{4.5}Cl^{3.5}$ |
| Chlonaphthalane A | $C^{10}H^{5.5}H^{2.5}$ |
| Chlorebronaphtine | $C^{10}H^{5.5}Br^{.5}Cl^{2}$ |
| Bromide of chlorebronaphtine | $C^{10}H^{5.5}Br^{4.5}Cl^{2}$ |
| Chlorenbronaphtone B | $C^{10}H^{4.5}Br^{2}Cl^{1.5}$ |
| Bromenchlonaphtose A | $C^{10}H^{4}Br^{1.5}Cl^{2.5}$ |
| Bromanchlonaphtone A | $C^{10}H^{4.5}Br^{.5}Cl^{3}$ |
| Bromochlonaphtune B | $C^{10}BrCl^{3.5}H^{3.5}$ |

Laurent's vowel system of nomenclature can only be applied with difficulty to such combinations as the above.

***Chloronaphthalic acid***, $C^{10}H^{5}ClO^{3}$. When tetrachloride of chloronaphthalene is boiled with nitric acid, and ether poured on the oily product, chloride of chloroxynaphthalene is precipitated, and may then be boiled with alcoholic potash in which it is completely soluble. On diluting with a small quantity of water and neutralising with an acid, chloronaphthalic acid crystallises out on cooling (Laurent). According to Wolff and Strecker, this process, instead of yielding the ordinary yellow barium-salt, sometimes gives a purple-red salt, possibly of a more highly chlorinated chloronaphthalic acid.

The acid forms long, yellow, transparent needles, unaffected by exposure to the air. Melts about 200°, and on cooling crystallises in laminæ. Distils without decomposition. Has the same formula as chloroalizarin.—Nitric acid converts it into phthalic and oxalic acids.—It is not reduced to alizarin by potassium-amalgam or by the voltaic battery.

*Chloronaphthalate of ammonium* forms radiated crimson needles. The *potassium-salt* forms carmine coloured needles, containing when dried at 100°, 18·07 per cent. $K^{2}O$. The *barium-salt*, $C^{10}H^{4}ClBaO^{3}$, prepared by precipitating a solution of the ammonium-salt with chloride of barium, crystallises in orange-coloured silky needles. The *strontium-salt* forms orange-yellow needles; the *calcium-salt*, orange-coloured needles. The *aluminium-salt* is an orange-coloured precipitate; the *cadmium-salt* is a vermillion-coloured precipitate which under the microscope appears in cruciform crystals; the *cobalt-salt*, a crimson precipitate becoming brown on drying, vermillion-coloured under the burnisher. The *copper-salt* is a crystalline crimson-coloured precipitate; the *ferric* and *ferrous salts* are brown precipitates; the *lead-salt* a gelatinous orange-red precipitate; the *silver-salt* a gelatinous blood-red precipitate. When prepared with heat, it forms a carmine-coloured crystalline precipitate. *Mercury-salts*. With solution of corrosive sublimate, a solution of chloronaphthalate of ammonium gives a reddish-brown precipitate.

Chloronaphthalic acid almost rivals turmeric and litmus in its sensibility to the presence of alkalis. Paper stained with an alcoholic solution (very dilute), if exposed to ammoniacal vapours, instantly assumes a more or less deep red colour.

### *Nitro-compounds of Naphthalene.*

***Nitronaphthalene***, $C^{10}H^{7}NO^{2}$. *Preparation.*—By far the most convenient method of preparing nitronaphthalene is to expose naphthalene to the prolonged action of cold nitric acid of moderate strength. For this purpose the hydrocarbon in small pieces or crystals is to be placed on the surface of nitric acid, of specific gravity 1·33. Large shallow evaporating basins are the most suitable vessels for the purpose. Six pts. nitric acid will suffice to convert 1 pt. of naphthalene. After exposure for some time, it will be found that the naphthalene has fused into a cake. It may then be cut with a piece of sheet glass or a platinum knife into small pieces which, after draining on a funnel, may be broken up in a mortar and returned to the acid. This is to be repeated as often as the mass becomes caked, about a week being required to complete the process. No red vapours of any consequence are evolved, and there are no secondary products formed. When the action is completed, the product is to be broken small and drained on a funnel until no more acid liquor falls. It may then be washed with cold water. The final purification may be effected by one or two crystallisations from boiling methylated spirit. By this process even hundredweights may be prepared with the greatest ease.

*Properties.*—Pale yellow prismatic needles derived from prisms of 100° and 80°, the acute angles being truncated. Melts at 43°, the temperature rising to 54° at the moment of solidification. Volatilises almost without decomposition, if carefully heated. If the heat be applied rapidly, it decomposes with ignition and deposition of carbon.

*Decompositions.*—1. *Ferrous acetate* reduces it to naphthylamine, as also does *sulphide of ammonium* (see NAPHTHYLAMINE).—2. *Sulphite of ammonium* converts it into naphthionic and thionaphthamic acids.—3. Heated with 7 or 8 times its weight of *hydrate of calcium* or *barium*, it yields Laurent's naphtase.—4. *Chlorine* aided by heat converts it into an oil which, when treated with potash, yields the *a* modification of trichloronaphthalene, or sometimes tetrachloronaphthalene.—5. *Bromine* aided by heat yields hydrobromic acid and dibromonaphthalene.—6. *Fuming sulphuric acid* converts it into nitrosulphonaphthalic acid.—7. Heated in a water-bath with a part of 2 pts. *hydrate potassium* and 1 pt. fresh *hydrate of calcium*, as little water as possible being used, it decomposes completely, yielding the potassium-salt of nitrophthalic acid.—8. When it is heated in a retort with *hydrate of potassium* and *slaked* lime to a temperature of 140°, and oxygen passed over it, the gas is slowly absorbed and the mixture becomes yellow. The operation takes ten or twelve hours, at the end of which time the oxidation of the nitronaphthalene is almost complete. The alkalis have then entered into union with a substance which Dusart calls nitroxynaphthalic acid. (See NITROXYNAPHTHALIC ACID.)

*Dinitronaphthalene*, $C^{10}H^6N^2O^4$.—Naphthalene or nitronaphthalene may be converted into this compound by long boiling with nitric acid. The operation is to be continued until the oily layer solidifies entirely on cooling, the product being washed on a glass funnel with water, and crystallised from alcohol. It forms very small needles which crystallise from a solution in nitric acid in rhombic prisms of 67° and 113°. Melts at 185°, and may be sublimed in small needles. When suddenly heated, it decomposes violently, with ignition and deposition of carbon. By prolonged boiling it is converted into trinitronaphthalene. *Chlorine* produces di- and trichloronaphthalene. *Sulphide of ammonium* converts it into seminaphthylamine. A feebly ammoniacal boiling solution is reduced by sulphide of hydrogen to ninaphthylamine (Wood). Its alcoholic solution is converted into nitrosonaphthylin in contact with *zinc* and *hydrochloric acid*. (Perkin and Church.)

*Trinitronaphthalene*, $C^{10}H^5N^3O^6$.—This compound exists in three forms, *α*, *β* and *γ*.

*Modification α.*—When naphthalene is boiled for a day or two with strong nitric acid, colourless crystals are formed which are a mixture of dinitronaphthalene and trinitronaphthalene, *α* and *β*. The dinitronaphthalene and a substance called by Laurent *nitronaphthaleïse* may be removed by ether. The residue is to be boiled with only enough alcohol to dissolve half of it. By spontaneous evaporation the trinitronaphthalene *α* will be obtained mixed with needles which may be removed by agitating the liquid and pouring off the suspended crystals.

Rhombic tablets, pale yellow, inodorous and only very slightly soluble in boiling alcohol. Volatile without decomposition when carefully heated, but decomposing with violence when heated rapidly. Melts at 210°, and solidifies into a fibrous mass on cooling.

Chlorine first turns it red and then decomposes it. Alcoholic potash in solution evolves ammonia, yielding a red solution from which acids precipitated brown or black flocks.

*Modification β.*—The residues of the preparation of modification *α* are to be mixed, and boiled with nitric acid for 5 or 6 days. On cooling needles are obtained which are to be washed first with nitric acid, then with water, and finally with alcohol. They are colourless at first, but become yellow by exposure; melt at 215°; decompose with ignition when heated in close vessels; very slightly soluble in boiling alcohol or ether, less so in fact than any other of the nitronaphthalenes.

Boiling alcoholic potash turns the compound orange-red at first, then brown. Acids precipitate from the alkaline solution a brown substance. Boiling nitric acid decomposes it according to Laurent, which is strange, considering its mode of formation.

*Modification* $\gamma$, called also *Marignac's Trinitronaphthalene.* This substance constitutes the chief part of the insoluble residue remaining when dinitronaphthalene is prepared by boiling naphthalene with nitric acid without the aid of fuming sulphuric acid. This residue is to be washed with water and extracted by cold ether which dissolves the trinitronaphthalene $\gamma$, and yields it on evaporation as an adhesive resinous mass.

It is pale yellow, crystallises in a pulverulent form from a solution in boiling alcohol. Melts below 100°. Almost insoluble in boiling ether, and only sparingly soluble in boiling alcohol. When carefully heated it sublimes, but if the heat be applied rapidly it decomposes with explosion. Solutions of the caustic and carbonated alkalis dissolve it with a fine red colour, the solution gradually becoming black. From the alkaline solution acids precipitate brown flocks, having, according to Marignac, the formula $C^{12}H^{3}NO^{8}$.

Laurent has described several other compounds derived from the nitronaphthalenes by substitution of one or more atoms of hydrogen by bromine and chlorine; they are not however of any very special interest.

### *Sulphuric derivatives of Naphthalene.*

For the numerous products of the action of sulphuric acid upon naphthalene, see SULPHONAPHTHALIC ACID.

### *Products of oxidation of Naphthalene.*

The following products of oxidation of naphthalene will be found under their proper headings, NAPHTHALASE, NAPHTHESIC ACID, NAPHTHULMIN.

### *Uses of Naphthalene.*

The enormous quantities of naphthalene which are produced during the distillation of coal-tar are seldom or never extracted from the 'pitch oil.' Great efforts have been made to find a use for it, but none have been entirely successful. Lamp black is sometimes prepared by condensing the dense smoke which burning naphthalene evolves.

A French surgeon, M. Emery, has employed naphthalene in the treatment of certain skin diseases. He tried it on fourteen patients in the hospital of St. Louis, and twelve were cured. In the two cases which failed one was a woman 30 years of age, who had been afflicted for eight years with *psoriasis gyrata*; the other was a young man who had suffered for eight years with *lepra vulgaris.* The latter case was cured by a two months' course of pitch ointment. The mode in which M. Emery applied the naphthalene was in the form of ointment in the strength of ʒss to ʒi of lard. The inflammation which sometimes supervenes must be combated by poultices.

Great efforts have also been made to produce fast colours from naphthalene, but up to the present time the results have not been successful. There is no doubt whatever that in a few years, perhaps in a few months, the difficulties in the way of utilising naphthalene will be overcome.

The action of reducing agents, such as zinc and hydrochloric acid, upon dinitronaphthalene gives rise to nitrosonaphthylin, a beautiful colouring matter. The same compound also affords colours when heated with stannous chloride and cyanide of potassium. The close relations which appear to exist between the formulæ of alizarin and some of the derivatives of naphthalene have long led to a hope of the artificial formation of the former substance. Indeed M. Roussin, by reducing dinitronaphthalene with sulphuric acid and zinc, produced a colouring matter which was for some time considered to be alizarin; subsequent researches however showed that the conclusions which had been formed regarding M. Roussin's substance were too hasty. In fact naphthazarin yields only sombre shades, which have not been found of industrial importance.

The beautiful substance obtained by Messrs. Perkin and Church by acting upon a salt of naphthylamine with nitrite of potassium, and to which they have given the name of azodinaphthyldiamine (see NAPHTHYLAMINE), yields superb-coloured derivatives, some of which can easily be applied to tissues; they have not yet however been successfully fixed.
C. G. W.

**NAPHTHALIN.**
**NAPHTHALINE.** } Syn. with NAPHTHALENE.

**NAPHTHALO-CYANIC** and **NAPHTHALO-SULPHOCYANIC ACIDS.** Syn. with CYANATE and SULPHOCYANATE OF NAPHTHYL (p. 19).

**NAPHTHAMEINE.** Syn. with OXYNAPHTHYLAMINE.

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**NAPHTHESIC ACID.** $C^{10}H^8O^4$. *Preparation.*—According to Laurent, when naphthalene is treated with acid chromate of potassium, water, and sulphuric acid, a violent reaction takes place and naphthesic acid (and sometimes a rose-coloured substance, *carminaphthone* $C^{10}H^4O^3$ ?) is formed. The mass, after the reaction is over, is to be treated with water and thrown on a filter. The solution, after the lapse of a considerable time (two months), deposits crystals of chrome-alum, which in time become covered with white warty granules. The latter are to be dissolved in alcohol, and the solution after filtration is to be evaporated, when the naphthesic acid will remain as a crystalline mass.

*Properties.*—Rhombic needles of 58° and 122°. Melts below 100° and may be sublimed at a higher temperature. Soluble in alcohol, almost insoluble in water.

C. G. W.

**NAPHTHIONIC ACID.** $C^{10}H^9N.SO^3$. *Sulphonaphthalidamic acid.* (Piria, Ann. Chim. Phys. [3] xxxi. 217; Gm. xiv. 110; Gerh. iii. 469.)

*Preparation.*—One part of nitronaphthalene, after being washed with water until the nitric acid used in its preparation is removed, is warmed with 5 parts of alcohol until dissolved; and 5 parts of solution of sulphite of ammonium, specific gravity 1·24, are added. The mixture, if kept gently boiling, deposits acid sulphite of ammonium, and acquires an acid reaction. Carbonate of ammonium in powder is then to be added until the acid reaction disappears. After boiling a short time the acid reaction again becomes apparent, and must be destroyed as before. The boiling is continued until no turbidity is observed on adding a drop of the liquid to water. The liquid forms two strata, the upper containing thionaphthamate and naphthionate of ammonium, and the lower sulphite and sulphate. The upper layer is to be separated and evaporated over a lamp to an oily consistence and then put aside. After some time it becomes converted into a mass of orange-yellow crystals of thionaphthamate of ammonium. The mother-liquid, which contains the naphthionate of ammonium, is heated to 100° and mixed with hydrochloric acid, which precipitates the naphthionic acid. It is now to be washed with water and with alcohol, until the liquids come away colourless. The naphthionate of ammonium is then to be converted into a calcium or sodium-salt, which may be purified by repeated crystallisations; and, when it has become colourless, it is once more dissolved in water and precipitated by a slight excess of hydrochloric acid. The acid thus precipitated is washed with water and then with alcohol. As moist naphthionic acid is easily altered by contact with air, it is necessary that the water used for washing it be freed from air by prolonged ebullition.

*Properties.*—As precipitated from a warm solution, naphthionic acid forms small light colourless crystals resembling asbestos. It is tasteless and inodorous; reddens litmus paper. It is only slightly soluble in water, 2000 parts of the latter dissolving only 1 part at ordinary temperatures. It is only slightly soluble in *alcohol.* It completely saturates alkalis, but its salts with heavy metals have an acid reaction. It evolves acetic acid from acetates even at ordinary temperatures. The crystals are rendered anhydrous by a temperature of 100°.

*Decompositions.*—1. *Heated* on platinum, it burns and evolves sulphurous acid, giving off an inflammable vapour having an odour recalling that of bitter almonds; it leaves a large carbonaceous residue.—2. Moist naphthionic acid is decomposed by exposure to the air.—3. It is not decomposed by boiling with concentrated hydrochloric acid. —4. *Concentrated sulphuric acid* dissolves it with the aid of heat. The solution is transparent and colourless; it may be heated to nearly 200° without decomposition, but about 220° it begins to blacken and give off vapours of sulphuric acid.—5. Concentrated solution of *hydrate of sodium* does not attack it.—6. *Dilute nitric acid* is without action on it, but when concentrated, especially if it contains *nitrous acid*, it converts it into a brown resin.—7. *Chlorine* passed into a solution of a naphthionate turns it brown and precipitates a resinous substance.—8. *Acid chromate of potassium* aided by heat acts like chlorine. The presence of sulphuric acid accelerates the decomposition.

Salts of Naphthionic Acid.—The naphthionates are all soluble, and crystallise easily from a solution in weak alcohol. Solutions of naphthionates are opalescent, and when viewed at different angles transmit beautiful red, blue and violet colours. Excessively weak solutions produce these effects, a solution of naphthionate of sodium containing only $\frac{1}{200,000}$ of salt being capable of showing the phenomenon.

The aqueous solutions of the naphthionates of the alkali-metals are not precipitated by *acetic acid* even when heated; but the alcoholic solutions treated with acetic acid yield a small precipitate of naphthionic acid.—*Ferric chloride* added to a solution of naphthionate of sodium, gives an abundant brick-red precipitate which turns brown when heated.—*Platinic chloride* gives a yellow precipitate.—*Nitrate of silver* gives a white crystalline precipitate. *Trichloride of gold* turns the solution of naphthionate of sodium purple, and gives a precipitate of metallic gold.—*Mercuric chloride* affords a white precipitate.—*Sulphate of copper* turns the solution yellow, but gives no precipitate.

*Naphthionate of Ammonium.*—Very soluble in water and alcohol; crystallises with difficulty.

*Naphthionate of Barium.*—This compound is best prepared by double decomposition of a solution of naphthionate of sodium with chloride of barium; for this purpose 2 parts of naphthionate of sodium and 1 part of chloride of barium are to be dissolved in 10 parts of boiling water. The naphthionate of barium crystallises out on cooling, and may be rendered perfectly pure by two recrystallisations from boiling water.

Two different kinds of crystals of this salt may be prepared by regulating the temperature at which the solution crystallises. If a small quantity of liquid be employed, micaceous laminæ form in the fluid while still warm. The crystals so formed have a slightly violet tint. If the solution, on the other hand, is more dilute, it does not begin to crystallise until after complete cooling; the salt then assumes the form of large transparent rhombohedral laminæ. It is moderately soluble in water.

*Naphthionate of Calcium*, $C^{10}H^8CaN.SO^3.4H^2O$.—When crude naphthionic acid is boiled with milk of lime, the filtered solution evaporated over the water-bath, and then left at rest, bulky reddish crystals are deposited which may be purified by washing on a funnel with cold alcohol, which dissolves resinous impurities. The salt thus partially purified is to be dissolved in boiling water, decolorised by animal charcoal and set aside to crystallise. It crystallises in white semi-transparent laminæ having a fatty appearance. Individual crystals appear colourless, but when seen in masses they possess a very beautiful rosy tint. Very soluble in water, almost insoluble in alcohol. It has no action on vegetable colouring matters.

*Naphthionate of Lead*, $C^{10}H^8PbNSO^3.H^2O$, prepared by double decomposition of a solution of naphthionate of sodium with nitrate of lead.—Forms short reddish needles, slightly soluble in water, but insoluble in alcohol. Reddens litmus. It is altered by boiling with water, the solution becoming red and gradually losing its power of crystallising.

*Naphthionate of Magnesium*, $C^{10}H^8MgNSO^3$.—Easily obtained by boiling for about two hours a mixture of 2 pts. of crude naphthionic acid and 1 pt. of carbonate of magnesium with water. The solution is to be filtered and set aside to crystallise. It is to be purified by recrystallisation from weak alcohol. If the solution be concentrated, the resulting salt will contain 4 atoms of water of crystallisation; but if the mother-liquor be allowed to evaporate spontaneously *in vacuo*, the crystals will contain 5 atoms of water.

*Naphthionate of Potassium*, $C^{10}H^8KNSO^3$.—This salt is anhydrous, very soluble in water and alcohol, but sparingly soluble in the same liquids when hydrate of potassium is present. It is easily obtained by dissolving crude naphthionic acid in a boiling concentrated solution of hydrate of potassium. It crystallises out on cooling in small micaceous laminæ.

*Naphthionate of Silver*, $C^{10}H^8AgNSO^3.H^2O$, obtained by decomposing a perfectly neutral solution of nitrate of silver with a solution of naphthionate of sodium, is a white curdy powder, sometimes becoming converted into dense crystalline grains with an adamantine lustre. Little soluble in cold water, more so in hot. Becomes grey on exposure to light.

*Ammoniacal naphthionate of Silver*, $C^{10}H^8AgSO^3.2NH^3.2H^2O$, is deposited in white crystalline grains, on treating a hot solution of the last-described salt with ammonia and leaving the liquid to cool. It is but slightly acted upon by light.

*Naphthionate of Sodium*, $C^{10}H^8NaNSO^3.4H^2O$.—This salt may be prepared by dissolving crude naphthionic acid in hot alcohol, with addition of powdered carbonate of sodium. The boiling solution, after filtration and repose, yields fine nearly colourless prisms of the salt. It may be purified by being reduced to powder and washed on a funnel with a concentrated alcoholic solution of hydrate of sodium; after this it must be dissolved in alcohol, and decolorised by animal charcoal. After the latter treatment it will be necessary to recrystallise it several times.—The salt forms fine prisms belonging to the monoclinic system, very slightly soluble in alkaline liquids, and readily soluble in water and alcohol, insoluble in ether. When in masses the crystals always appear yellow. The crystals are at first insipid, but afterwards yield a sweet persistent taste. The salt serves for the preparation of several of the naphthionates by double decomposition.—When heated, it yields a residue of sulphate and much carbon.—It is not changed by exposure to dry air.

*Naphthionate of Zinc*, $C^{10}H^8ZnNSO^3$.—Obtained by double decomposition of naphthionate of sodium with sulphate of zinc. It forms large red laminæ, transparent but becoming opaque at 90°, with loss of some of its water of crystallisation. Very soluble in water, soluble in anhydrous alcohol with the aid of heat. Becomes anhydrous between 150° and 160°.

C. G. W.

**NAPHTHULMIN.** $C^{10}H^{8}O^{2}$. (Schützenberger and Willm, Compt. rend. xlvi. 894.)—A substance produced together with azodinaphthyldiamine (p. 23) by the action of aqueous nitrite of potassium on hydrochlorate of naphthylamine. The azodinaphthyl-diamine may be dissolved out by alcohol or ether, and naphthulmin then remains as a black, rather bulky, humus-like substance, insoluble in nearly all solvents, especially in acids and alkalis. It dissolves however in strong sulphuric acid, forming an indigo-coloured solution whence it is precipitated by water.

**NAPHTHYL.** $C^{10}H^{7}$.—The monatomic radicle of naphthylamine, &c.

*Cyanate of Naphthyl*, $C^{11}H^{7}NO = \left.\begin{matrix}CN\\C^{10}H^{7}\end{matrix}\right\}O$, is produced in small quantity by heating dinaphthyl-carbamide with phosphoric anhydride (V. Hall, Phil. Mag. [4] xvii. 304), probably also when menaphthoximide is heated to 260° (Perkin, Chem. Soc. J. ix. 8). It forms magnificent easily fusible crystals, insoluble in water, easily soluble in alcohol and ether. Its reactions are exactly analogous to those of cyanate of phenyl (ii. 196). (Hofmann, Compt. rend. xlvii. 425.)

*Sulphocyanate of Naphthyl*, $C^{10}H^{7}NS = \left.\begin{matrix}CN\\C^{10}H^{7}\end{matrix}\right\}S$. Obtained, together with naphthylamine, by distilling dinaphthylsulpho-carbamide with phosphoric anhydride:

$$\left.\begin{matrix}(C^{10}H^{7})^{2}\\(CS)''\\H^{2}\end{matrix}\right\}N^{2} = \left.\begin{matrix}CN\\C^{10}H^{7}\end{matrix}\right\}S + \left.\begin{matrix}C^{10}H^{7}\\H^{2}\end{matrix}\right\}N.$$

It forms splendid, easily fusible crystals, having a peculiar odour, insoluble in *water*, very soluble in *alcohol* and *ether*. When boiled in alcoholic solution with naphthylamine, it is reconverted into dinaphthyl-sulphocarbamide. With *aniline* it forms sulphocyanate of phenyl-naphthylamine: $\left.\begin{matrix}CN\\C^{10}H^{7}\end{matrix}\right\}S + \left.\begin{matrix}C^{6}H^{5}\\H^{2}\end{matrix}\right\}N = \left.\begin{matrix}CN\\C^{10}H^{9}(C^{6}H^{6})N\end{matrix}\right\}S.$ (Hall, Hofmann; *loc. cit.*)

**NAPHTHYLAMINE.** $C^{10}H^{9}N$. *Naphthalidam, Naphthalamine, Naphthalidine.* (Zinin, J. pr. Chem. xxvii. 143; abstr. Ann. Ch. Pharm. xliv. 283. Piria, Ann. Ch. Phys. [3] xxxi. 217. Béchamp, *ibid.* xlii. 186. Delhos, *ibid.* xxi. 68. W. H. Perkin, Chem. Soc. Qu. J. ix. 8; Chem. Gaz. 1856, p. 119. Hugo Schiff, Ann. Ch. Phys. lii. 112. A. W. Hofmann, Compt. rend. xlvii. 425; Ann. Ch. Phys. [3] liv. 204. Schützenberger and Willm, Compt. rend. xlvii. 82. Perkin and Church, Chem. Soc. J. xvi. 207.—Discovered by Zinin in 1842 during his important researches on the reduction of nitro-compounds.

*Preparation.*—Zinin's process consists in mixing 1 pt. nitronaphthalene with 10 pts. of strong alcohol, and saturating the mixture first with ammonia and then with sulphide of hydrogen. The essential features of the reaction are expressed by the annexed equation:

$$\underset{\text{Nitronaphthalene.}}{C^{10}H^{7}NO^{2}} + 3H^{2}S = \underset{\text{Naphthylamine.}}{C^{10}H^{9}N} + 2H^{2}O + S^{3}.$$

Piria's process consists in taking advantage of the ease with which the thionaphthamates are converted into naphthylamine. When the thionaphthamate of an alkali is treated with dilute sulphuric acid and the solution is heated, sulphate of naphthylamine is produced in accordance with the equation—

$$\underset{\text{Thionaphthamic acid.}}{2C^{10}H^{9}NSO^{3}} + H^{2}O = 2(C^{10}H^{9}N)H^{2}SO^{4}.$$

3. According to Piria, naphthylamine is also produced by distilling a thionaphthamate with excess of hydrate of calcium.

4. The process almost invariably used at the present day is, however, that of Béchamp, which consists in reducing nitronaphthalene with iron filings and acetic acid. According to Schützenberger and Willm, phthalamine, $C^{8}H^{4}NO^{2}$, is also formed in this reaction. The production of naphthylamine by Béchamp's process is precisely analogous to that of aniline from nitrobenzene with the same reagents, and may be written thus:

$$C^{10}H^{7}NO^{2} + 6Fe^{2}O + H^{2}O = 3Fe^{4}O^{3} + C^{10}H^{9}N.$$

It is quite unnecessary to give at length all the modifications of Béchamp's process, which have been described by various operators. The following method of preparation will be found to answer either on the large or on the small scale: 1 pt. of nitronaphthalene which has been well washed with water to remove adhering nitric acid, is mixed with 1½ pt. of iron filings, and commercial acetic acid is added in sufficient quantity to cover the whole. The retort must be very capacious, and should be able to hold at least ten times the quantity of the ingredients taken. A gentle heat is applied until the nitronaphthalene melts. The reaction soon sets in, and is generally very active, the contents of the retort frothing violently, and boiling over unless the fire is removed. As soon as the frothing has subsided, the retort is to be cautiously heated until the acetic acid has distilled over, after which it is to be removed from the fire and allowed to cool. A strong solution of hydrate of potassium may then be added, until the mixture, after being well stirred, is powerfully alkaline. The retort may now be transferred to a deep sand-bath and covered with sand up to the neck. The fire is to be urged until the naphthylamine comes over, which however will not be the case until the temperature has risen to 300°. The oily naphthylamine thus obtained is purified by solution in hydrochloric acid; the filtered liquid is evaporated to dryness and distilled with hydrate of calcium; the base then passes over in the form of a colourless oil contaminated only by the presence of phthalamine. The latter may be removed by converting the mixture of bases into sulphates and crystallising. The sulphate of naphthylamine being less soluble than sulphate of phthalamine, will crystallise out first.

Roussin prepares naphthylamine by treating nitronaphthalene with tin and hydrochloric acid. He introduces into a balloon (which should have twice the capacity necessary for holding the ingredients) 6 pts. of commercial hydrochloric acid, 1 pt. of nitronaphthalene, and as much granulated tin as will reach to the surface of the mixture. The balloon is heated in a water-bath and shaken at intervals. An energetic reaction is soon set up, the nitronaphthalene disappears, and the mixture, which is of a brown colour, becomes transparent. The product in this condition is poured into an earthenware vessel containing two litres of commercial hydrochloric acid diluted with half its bulk of water. The hydrochlorate of naphthylamine soon begins to crystallise, and finally renders the whole solid. On cooling, the magma is drained on linen filters, and subsequently pressed. To purify the crude hydrochlorate prepared in this manner, it is, after drying, to be dissolved in boiling water and treated with a sufficient quantity of solution of sulphide of sodium to precipitate the tin. The liquid is then passed through a wet paper filter to remove a tarry impurity. The pure hydrochlorate crystallises on cooling. The base may be separated by the addition of an alkali.

*Properties.*—Naphthylamine precipitated from a solution of the sulphate by ammonia forms white silky needles. As ordinarily obtained by distillation, it is a yellowish-white crystalline mass. It melts at 50°, and distils at about 300° without decomposition. In spite of this fact its vapour-density does not appear to have been determined. If very slowly heated it sublimes in long silky needles. It has a most disgusting and persistent odour, which adheres to the hands and clothes for a long time. Some persons appear to be injuriously affected by it when working with it for some time (Carey Lea). Solutions of naphthylamine colour deal-wood yellow even more intensely than aniline. (Hofmann.)

*Decompositions.*—1. Naphthylamine burns with a smoky flame, leaving a residue of carbon (Zinin).—2. Turns violet in the air (Zinin). This violet substance appears to be produced during the formation of naphthylamine from nitronaphthalene by Béchamp's process; one or two grains are all that can be obtained from 50 or more grammes of nitronaphthalene (Carey Lea). Sublimed naphthylamine becomes coloured only after long exposure to the air and sunlight, and if protected from these influences may be kept unaltered for years (Zinin).—3. Heated to 200° with dry *mercurous nitrate* it yields, according to the quantities of salt employed, various shades of colour from that of aniline-violet to that of fuchsine (Scheurer-Kestner).—4. *Stannic chloride* converts it into a red colour (Kestner).—5. Not attacked by *chlorine* in the cold, but violently when in a melted state, hydrochlorate of naphthylamine and a resinous substance being formed (Zinin).—6. Solution of hydrochlorate of naphthylamine treated with *chlorine* affords a violet colour, a brown resin, and a substance crystallising in golden-yellow needles (Zinin).—7. With *ferric chloride*, *nitrate of silver*, *trichloride of gold* and oxidising substances generally, it gives an azure-blue precipitate of naphthameïne (Piria).—8. When *nitrite of potassium* is added to a solution of a salt of naphthylamine, a reddish-brown precipitate is immediately produced called by its discoverers azodinaphthyldiamine, and having the formula $C^{20}H^{15}N^{3}$ (Perkin and Church).—9. *Platinic chloride*, *mercuric chloride*, and *chloride of zinc* yield the naphthameïne of Piria which appears in fact to be oxynaphthylamine (Schiff). This is probably also the substance obtained by heating nitronaphthalene with the hydrates of potassium and calcium.—10. *Nitric acid*, especially if it contains *nitrous acid*, converts naphthylamine into a brown powder, almost insoluble in water, but soluble in alcohol with the production of a violet liquid (Zinin). Inasmuch as the last reaction is favoured by the presence of nitrous acid, it is probable that the resulting product is (or at least contains) Perkin and Church's azodinaphthyldiamine. This is rendered the more probable because, according to Zinin, the product of the action of *nitric acid* is obtained, on evaporating its solution, in the form of crystals resembling murexide, and azodinaphthyldiamine crystallises in magnificent green crystals having somewhat the appearance of murexide, but much larger and finer.—11. A mixture of *nitric and sulphuric acids* acts violently on naphthylamine; on the addition of water to the mixture flakes are deposited which are probably nitronaphthylamine, $C^{10}H^8(NO^2)N$.—12. *Oxychloride of phosphorus* converts naphthylamine into trinaphthylphosphamide (Schiff).—13. A solution of *acid chromate of potassium* added to a solution of a salt of naphthylamine yields a precipitate containing a violet colouring matter.—14. A solution of naphthylamine in anhydrous ether when treated with *gaseous cyanic acid*, affords naphthyl-urea, $C^{11}H^{10}N^2O$; under certain circumstances the reaction proceeds differently, and colouring matters are formed (Schiff).—15. An alcoholic solution of naphthylamine combines with *oil of mustard*, forming allyl-naphthyl-sulphocarbamide, $C^{14}H^{14}N^2S^2$ (Zinin).—16. With *sulphocyanate of phenyl*, phenyl-naphthyl-sulphocarbamide is produced (Hofmann).—17. When an alcoholic solution of naphthylamine is treated with *disulphide of carbon*, or when it is heated in a sealed tube with that reagent, dinaphthyl-sulphocarbamide is produced (Laurent, Delbos, Schiff).—18. When fused naphthylamine is treated with *gaseous chloride of cyanogen*, heat is given off and hydrochlorate of menaphthylamine, $C^{21}H^{17}N^3.HCl$, is formed (Perkin).—19. With the iodides &c. of the alcohol-radicles, methyl-naphthylamine, ethyl-naphthylamine, &c., are formed. (Schiff.)

### SALTS OF NAPHTHYLAMINE.

***Bromhydrate*** or ***Hydrobromate***, $C^{10}H^9N.HBr$.—Obtained by decomposing a concentrated alcoholic solution of sulphate of naphthylamine with bromide of potassium or barium. The solution filtered from the sulphate of barium is to be slowly evaporated. Crystalline salt, readily soluble in alcohol, moderately soluble in water.

***Chlorhydrate*** or ***Hydrochlorate***, $C^{10}H^9N.HCl$.—When a strong solution of naphthylamine in alcohol is mixed with hydrochloric acid, the whole solidifies to a mass of hydrochlorate of naphthylamine, consisting of small shining scales, rather freely soluble in water, and still more so in alcohol and ether. It sublimes at about 200° with only slight decomposition; the sublimate consists of very fine needles. Like the sulphate, the dry salt is not decomposed by exposure to the atmosphere, but the solution, or the crystals if wet, become rapidly decomposed, with production of a red colour.

***Chloromercurate.***—When a solution of mercuric chloride is added to an alcoholic solution of naphthylamine or of its salts, a curdy yellow precipitate is obtained; it is soluble with difficulty in cold alcohol, but is deposited from a boiling solution on cooling in crystals.

***Chloroplatinate.***—A yellow precipitate slightly soluble in cold water, still less soluble in alcohol and ether. It crystallises without alteration from a boiling aqueous solution (Gerhardt). On pouring an alcoholic solution of hydrochlorate of naphthylamine into a solution of platinic chloride, a green colour is developed, and the salt is deposited as a brownish green-yellow powder. (Zinin.)

***Nitrate***, $C^{10}H^9N.HNO^3$.—Naphthylamine dissolves without decomposition in weak boiling nitric acid if the latter be free from nitrous acid. The solution becomes however slightly reddish. On cooling brilliant scales are deposited of nitrate of naphthylamine.

***Oxalates.*** 1. *Neutral salt.*—Crystallises in stellar groups consisting of small laminae having the formula $2C^{10}H^9N.C^2H^2O^4$. It yields dinaphthylcarbamide on distillation.—2. *Acid salt*, $C^{10}H^9N.C^2H^2O^4$.—This salt forms in white warty masses, readily soluble in water and alcohol. When submitted to destructive distillation, it yields a brownish-yellow powder soluble in alcohol but insoluble in water.

***Phosphates.*** 1. *Orthophosphate.*—Naphthylamine treated with solution of phosphoric acid which has not been ignited, forms this salt, which is readily obtained in crystals even when dilute solutions of the base are treated with an aqueous solution of the acid. It rapidly turns red by exposure to the air.—2. *Metaphosphate.*—When an alcoholic solution of naphthylamine is treated with solution of metaphosphoric acid in alcohol, a white pulverulent salt is obtained. It is only slightly soluble in water and alcohol.

***Sulphate of Naphthylamine***, $2(C^{10}H^9N).H^2SO^4$, may be formed by dissolving the base in warm sulphuric acid. No crystals are obtained on cooling even to 0°, but, on dilution, the whole becomes nearly solid with small scales of the salt. The same salt may be obtained by adding sulphuric acid to a solution of thionaphthamate of potassium, sodium, or ammonium, and gently heating. It crystallises in white silvery scales having the disgusting odour of the base, and an acid reaction. When dry it may be kept without alteration, but the solution decomposes, with production of a red colour. When distilled it melts, gives off sulphurous acid, and leaves a residue of carbon. A small portion of the base distils over undecomposed (Zinin). It is only slightly soluble in cold water or alcohol, but freely so in hot alcohol.

Intimately connected with naphthylamine are the substances which Piria discovered by acting on nitronaphthalene with sulphite of ammonium. (See THIONAPHTHAMIC ACID and NAPHTHIONIC ACID.)

*Substitution-derivatives of Naphthylamine.*

*α. Bromide of Ethyl-naphthylammonium*, $C^{12}H^{14}NBr = (C^{10}H^7.C^2H^5.H^2)NBr$. —To prepare this compound, naphthylamine is treated with an excess of bromide of ethyl in a flask so connected with a Liebig's condenser as to allow the volatilised bromide to return, the temperature being maintained between 40° and 50° for some hours. The contents will at last be converted into a reddish-brown mass from which the excess of bromide of ethyl may be removed by distillation. The mass is then to be repeatedly exhausted with boiling water. The boiling solutions are to be filtered, and on cooling, the bromide of ethyl-naphthylammonium will crystallise out (Schiff).—2. Naphthylamine inclosed in a sealed tube with excess of bromide of ethyl and kept for fourteen days at ordinary temperatures, becomes almost entirely converted into crystals of the bromide. (Schiff.)

*Properties.*—Pale rose-coloured crystals which do not become colourless on recrystallisation. The salt does not become coloured so easily as naphthylamine. Very slightly soluble in cold water, but readily soluble in hot water, alcohol and ether. (Schiff.)

Heated with hydrate of potassium, the bromide gives naphthylamine and alcohol, in accordance with the equation—

$$N\left\{\begin{matrix}C^{10}H^7\\C^2H^5\\H^2\end{matrix}\right\}Br + KHO = N\left\{\begin{matrix}C^{10}H^7\\H^2\end{matrix}\right\} + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + KBr. \quad \text{(Schiff.)}$$

*β. Iodide of Methyl-naphthyl-ammonium.*—An attempt to prepare a methyl compound by treatment of naphthylamine with iodide of methyl failed, the product being a greasy mass which would not crystallise.

*γ. Sulphocyanate of Phenyl-naphthylammonium.* $C^{17}H^{14}N^2S = \left.\begin{matrix}CN\\C^{10}H^7(C^6H^5)N\end{matrix}\right\}S$.—Produced by the direct union of naphthylamine with sulphocyanate of phenyl, or of phenylamine with sulphocyanate of naphthyl (p. 19). It crystallises from its boiling solution in spangles very like diphenyl-sulphocarbamide; very soluble in alcohol and in ether. (Hofmann, Compt. rend. xlvii. 425.)

C. G. W.

**NAPHTHYL-CARBAMIDES.**—*α.* MONONAPHTHYL-CARBAMIDE or NAPHTHYL-UREA, $C^{11}H^{10}N^2O = \left.\begin{matrix}C^{10}H^7\\(CO)''\\H^3\end{matrix}\right\}N^2$. (See CARBAMIDES, i. 754.)

*β.* DINAPHTHYL-CARBAMIDE. *Carbonaphthalide*, $C^{21}H^{16}N^2O = \left.\begin{matrix}(C^{10}H^7)^2\\(CO)''\\H^2\end{matrix}\right\}N^2$. (Delbos, Ann. Ch. Phys. [3] xxi. 68.—Zinin, Ann. Ch. Pharm. cviii. 228).—Obtained, 1. By heating the neutral or acid oxalate of naphthylamine (Delhos). Dinaphthyloxamide, $C^{22}H^{16}N^2O^2$, is first formed, and afterwards resolved by increased heat, into carbonic oxide and dinaphthyl-carbamide.—2. By boiling dinaphthyl-sulphocarbamide with alcoholic potash (Delbos):

$$C^{21}H^{16}N^2S + H^2O = C^{21}H^{16}N^2O + H^2S.$$

3. By heating dinaphthyloxamide for a long time above its melting point, or submitting it to dry distillation (Zinin):

$$\left.\begin{matrix}(C^{10}H^7)^2\\(C^2O^2)''\\H^2\end{matrix}\right\}N^2 = \left.\begin{matrix}(C^{10}H^7)^2\\(CO)''\\H^2\end{matrix}\right\}N^2 + CO.$$

It is most advantageously prepared from acid oxalate of naphthylamine, which must be heated to complete fusion; the yellowish mass which distils over is then freed from naphthylamine by repeated boiling with alcohol.

Dinaphthyl-carbamide is a pure white, light and slightly silky mass, insoluble in *water*, very slightly soluble in boiling *alcohol*. It quickly turns red when exposed to the air, and distils with partial carbonisation at a temperature above 300°. When distilled with *phosphoric anhydride*, it yields cyanate of naphthyl, together with other products.

**NAPHTHYL-DIAMINES.** α. AZODINAPHTHYL-DIAMINE. $C^{20}H^{15}N^{3} = \left.\begin{matrix}(C^{10}H^{7})^{2}\\ N'''\\ H\end{matrix}\right\}N^{2}$ (Perkin and Church, Chem. Soc. J. xvi. 207).—A base produced by treating hydrochlorate of naphthylamine with nitrite and hydrate of potassium in the proportions indicated by the equation:

$$2(C^{10}H^{9}N.HCl) + KHO + KNO^{2} = C^{20}H^{15}N^{3} + 2KCl + 3H^{2}O.$$

A dark-coloured precipitate is thereby formed which when recrystallised once or twice from boiling alcohol, yields azodinaphthyl-diamine in splendid needles, having a bright green metallic reflection. It melts at 130° to a blood-red liquid having a green metallic lustre, and bears a considerable degree of heat without decomposition. It is insoluble in cold *water*; colours boiling water yellow; dissolves, but not very freely, in *alcohol*, *ether*, and *benzene*, even at boiling heat. Most *acids* colour the solutions deep violet; but the original orange-red tint is restored by alkalis, and even by water. *Oil of vitriol* colours the dry crystals dull green, changing to deep blue on addition of a trace of water. Strong *nitric acid* dissolves the base, forming a brown solution which afterwards changes to brownish-red, and water then throws down a brown precipitate.

Azodinaphthyl-diamine forms three *hydrochlorates*, viz. $(C^{20}H^{15}N^{3})^{4}.HCl$, crystallising in shining, golden-brown prisms; $C^{20}H^{15}N^{3}.HCl$, in dark purplish-red crystals; and $C^{20}H^{15}N^{3}.2HCl$, in bulky crystals yellow-brown by transmitted light, and having a green lustre when wet. The *sulphate*, $(C^{20}H^{15}N^{3})H^{2}SO^{4}$, forms greenish-brown crystals having a golden metallic lustre.

Azodinaphthyl-diamine boiled for some time with *potash* is partly reconverted into naphthylamine. By prolonged boiling with *hydrochloric acid*, it is slowly decomposed, yielding hydrochlorate of naphthylamine, and a substance soluble in potash. When treated with hydrochloric acid and granulated *tin*, it is decolorised and yields one or more new bases not yet examined. With *citraconic acid* it yields a solid substance probably consisting of azodinaphthyl-citraconamic acid.

By using a double proportion of nitrite of potassium, Perkin and Church (Chem. Soc. J. ix. 1) originally obtained a dark-coloured substance which they regarded as nitroso-naphthalene, $C^{10}H^{7}(NO)$; but subsequent experiments have shown that it was not a definite product, but merely impure azodinaphthyl-diamine.

*Benzoyl-azodinaphthyl-diamine*, $C^{27}H^{19}N^{3}O = C^{20}H^{14}(C^{7}H^{5}O)N^{3}$, is produced by heating azodinaphthyl-diamine with *chloride of benzoyl*. It forms brilliant red crystals, very stable and capable of melting without decomposition. It is insoluble in water, dissolves slightly in boiling alcohol, with yellow colour, which is darkened but not changed to violet by a large excess of hydrochloric acid. Dissolves in sulphuric acid with deep blue colour; is nearly insoluble in ether, but may be crystallised from benzene or from chloride of benzoyl. Dissolves, with orange colour, in alcoholic potash or soda, and is partially decomposed by continued boiling with potash followed by the action of hydrochloric acid.

The chlorides of *acetyl* and *cumyl* appear to form similar products with azodinaphthyl-diamine.

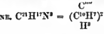
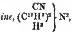
β. MENAPHTHYLAMINE, $C^{21}H^{17}N^{3}$, may be regarded as cyano-dinaphthyl-diamine (*vid. inf.*).

**NAPHTHYL-FORMAMIDE.** $C^{11}H^{9}NO = N.H(CHO)(C^{10}H^{7})$. See FORMAMIDE (ii. 681).

**NAPHTHYL-OXAMIDES.** See OXAMIDE.

**NAPHTHYL-PHOSPHAMIDE.** See PHOSPHAMIDE.

**NAPHTHYL-SULPHOCARBAMIDES.** See SULPHOCARBAMIDES.

**NAPHTHYL-TRIAMINES.** α. CARBODINAPHTHYL-TRIAMINE. MENAPHTHYLAMINE.  $C^{21}H^{17}N^{3} = \left.\begin{matrix}C''''\\ (C^{10}H^{7})^{2}\\ H^{3}\end{matrix}\right\}N^{3}$. (Perkin, Chem. Soc. Qu. J. ix. 8.)—This compound, which may also be regarded as *cyano-dinaphthyl-diamine*,  $\left.\begin{matrix}CN\\ (C^{10}H^{7})^{2}\\ H^{3}\end{matrix}\right\}N^{2}$, is formed as a hydrochlorate, by the action of chloride of cyanogen on naphthylamine ($2C^{10}H^9N + CNCl = C^{21}H^{17}N^3.HCl$), the mode of formation being precisely analogous to that of melaniline, or carbo-diphenyl-triamine, from aniline. To prepare it, gaseous chloride of cyanogen is drawn by an aspirator through a number of glass tubes partly filled with naphthylamine which is kept in fusion by the application of a gentle heat; the resulting black resinous mass, consisting chiefly of hydrochlorate of menaphthylamine, is boiled with a large quantity of water; the base is precipitated from the solution by ammonia or potash; and the precipitate is purified by washing with water, and one or two crystallisations from alcohol.

Menaphthylamine crystallises in small white needles, having a bitter taste, but no smell, nearly insoluble in *water*, soluble in *alcohol* and in *ether*. It becomes coloured in the air, and blues reddened litmus. It melts at about 200°, and decomposes at 260°, giving off naphthylamine and leaving a brown mass. It appears to form neutral compounds with *chlorine*, *iodine* and *bromine*. With *fuming sulphuric acid* it first forms a sulphate, but on heating the mixture, it liquefies and a new acid is produced which forms a soluble lead-salt.—*Fuming nitric acid* acts very slowly on menaphthylamine, forming a series of substitution-products. *Chromic acid* acts but slowly. *Cyanogen gas* passed through ether in which menaphthylamine is suspended, converts it into dicyanomenaphthylamine.

Menaphthylamine unites with *acids*, forming salts many of which are amorphous or but slightly crystalline. They are but sparingly soluble in water, and neutral to litmus-paper. They are precipitated by acids and by saline solutions; potash and ammonia added to their solutions precipitate the base as a pure white powder.

The *hydrochlorate*, $C^{21}H^{17}N^3.HCl$, is amorphous and very soluble in alcohol and ether. The *chloroplatinate*, $C^{21}H^{17}N^3.HCl.PtCl^2$, is deposited from alcoholic solutions in small yellow shining scales. The *chloro-aurate* is a blue precipitate. The *hydriodate*, *hydrobromate*, *phosphate* and *nitrate* are crystalline, the last forming small white prisms, and dissolve easily in alcohol and in ether. The *sulphate* is amorphous, and moderately soluble in alcohol and in ether.

*β*. DICYANO-MENAPHTHYLAMINE. $C^{23}H^{17}N^5 = C^{21}H^{17}N^3.Cy^2$.—Produced as above described by the action of gaseous chloride of cyanogen on menaphthylamine suspended in ether. It is pale yellow, crystallises with difficulty, is insoluble in water, moderately soluble in alcohol and in ether, dissolves easily in dilute acids, and is reprecipitated by ammonia if added immediately afterwards; but the solution, if left to itself for only a few seconds, becomes turbid and deposits cyanodinaphthyl-oxamide, $C^{23}H^{15}N^3O^2$. (Perkin, *loc. cit.*)

**NAPHTHYL-UREA.** Syn. with NAPHTHYL-CARBAMIDE.

**NAPLES YELLOW.** A basic antimonate of lead used in oil-painting. (See ANTIMONATES, i. 326.)

**NAPOLEONITE.** Syn. with orthoclase. (See FELSPAR, ii. 619.)

**NARCEINE.** $C^{23}H^{29}NO^9$. (Pelletier, Ann. Ch. Phys. l. 262.—Couerbe, *ibid.* lix. 151.—Anderson, Edinb. Phil. Trans. xx. Pt. 3, p. 347.)—An alkaloïd contained in opium. To prepare it, the aqueous extract of opium, from which morphine has been separated by Gregory's process (iii. 1051), is mixed with ammonia, which throws down narcotine, thebaine, and a resinous body. The liquid is filtered and mixed with acetate of lead; and the filtrate, after being freed from excess of lead by sulphuric acid, is neutralised with ammonia and evaporated till it becomes covered with a pellicle. It then on cooling deposits a crystalline mass, the quantity of which increases by repose. This mass is washed on a linen filter with cold water, and then dissolved in boiling water, which on cooling deposits crystals of narceine.

Narceine thus obtained sometimes contains sulphate of calcium; it may be purified by dissolving in alcohol, decolorising with animal charcoal, and recrystallising from water.

Narceine crystallises in elongated silky needles. It is inodorous, has a bitter and styptic taste, dissolves sparingly in cold, more readily in boiling *water*, is very soluble in *alcohol*, but insoluble in *ether*. The solutions of narceine slightly deflect the plane of polarisation of a luminous ray to the left; $[\alpha] = -6{\cdot}67°$.

Narceine melts at 92°, and solidifies in a crystalline mass on cooling. It turns yellow at 110°, and decomposes at higher temperatures. It is violently attacked by *chlorine* and *bromine*, yielding very complex products. *Iodine* forms with narceine a dark blue compound which is decomposed by boiling water.

*Potash*, *soda* and *ammonia* dissolve narceine, which, on concentrating the solutions, is deposited in the form of an oily liquid.

Strong mineral acids act powerfully on narceine and decompose it; the same acids when dilute combine with it and form salts.

The *sulphate* forms tufts of needles much resembling the free base. It is sparingly soluble in boiling water. The *nitrate* separates from a hot solution in radiating groups of crystals, sparingly soluble in cold water.

The *hydrochlorate*, $C^{23}H^{29}NO^{9}.HCl$ (at 100°) crystallises sometimes in concentrically grouped needles, sometimes in short irregular prisms. The crystals are very soluble in water and alcohol, and have an acid reaction. The *chloroplatinate*, $C^{23}H^{29}NO^{9}.HCl.PtCl^{2}$ (at 100°), gradually separates on adding platinic chloride to hydrochlorate of narceine, as a crystalline powder, or in small prismatic crystals (analysis, 41·0 per cent. C, 4·6 H, and 14·33—14·76 Pt; calc. 41·2 C, 4·5 H and 14·7 Pt).

**NARCETINE.** An alkaloïd produced by the action of sulphuric acid and peroxide of lead on narcotine. It is dissolved by strong sulphuric acid with a fine red colour, and by nitric acid with a fine yellow colour. By the prolonged action of the oxidising mixture it appears to be converted into opianic acid. (Marchand, Berz. Jahresber. xxv. 507.)

**NARCITINE.** A substance possessing emetic properties, contained in the white narcissus. (Jourdain, Rép. Pharm. [2] xxi. 338.)

**NARCOGENINE.** When a solution of narcotine in hydrochloric acid is boiled with platinic chloride, the product generally formed is chloroplatinate of cotarnine. Sometimes however another platinum-salt is formed, crystallising in long light yellow needles. This salt is supposed by Blyth (Ann. Ch. Pharm. l. 29) to be the chloroplatinate of a distinct alkaloïd, *narcogenine*. As however this salt is decomposed by ammonia into chloroplatinate of narcotine which is precipitated, and chloroplatinate of cotarnine which remains dissolved, it is probably merely a double salt composed of the chloroplatinates of narcotine and cotarnine.

**NARCOTEINE.** Syn. with NARCETINE.

**NARCOTIC ACID.** An acid said to be formed by boiling narcotine with potash. It appears to differ from narcotine only by the elements of water (p. 27).

**NARCOTINE.** $C^{22}H^{23}NO^{7}$. (Derosne, Ann. Chim. xlv. 257; Robiquet, Ann. Ch. Phys. v. 275; Dumas and Pelletier, *ibid.* xxiv. 188; Pelletier, *ibid.* l. 269; Liebig, Ann. Ch. Pharm. vi. 35; R. Brandes, *ibid.* ii. 274; Couerbe, Ann. Ch. Phys. lix. 159; Regnault, *ibid.* lxviii. 137; Wöhler, Ann. Ch. Pharm. l. 1; Blyth, *ibid.* l. 29; Wertheim, *ibid.* lxx. 71; lxxiii. 208; Anderson, *ibid.* lxxxvi. 179; Mattheissen and Foster, Phil. Trans. 1863, p. 345; Chem. Soc. J. xvi. 342.—Gm. xvi. 135; Gerh. iv. 67.)—This alkaloïd is contained in opium to the amount of 6 or 8 per cent., and was the first base extracted from that substance. It was discovered by Derosne in 1804, and went by the name of *Sel de Derosne*, till its basic character was demonstrated by Robiquet in 1807.

*Preparation.*—1. From the coloured uncrystallisable mother-liquors obtained in the preparation of morphine by Gregory's process (iii. 1051). These mother-liquors are diluted with water, filtered if necessary, and treated with ammonia as long as a precipitate continues to form; and the precipitate is collected on a cloth filter and pressed. It is granular at first, but becomes resinous if left under the press too long. It should therefore be quickly removed, suspended in water, and pressed again, the treatment being repeated several times. The precipitate contains narcotine together with a considerable quantity of resin and a little thebaine; the mother-liquor contains narceine and may be used for preparing that base. A portion of the precipitate is now to be boiled with rectified spirit and the solution filtered hot; on cooling it deposits strongly coloured crystals of narcotine, which are collected on a cloth, pressed, and washed with a little alcohol. The mother-liquor of these crystals serves to dissolve another portion of the precipitate, and in this manner the process is continued till the whole is dissolved. The impure crystals of narcotine are next rinsed with strong potash-ley, washed with water, and crystallised from boiling alcohol. The alcoholic liquor from which the first highly coloured crystals of narcotine were deposited, contains much resin, a little narcotine and all the thebaine of the opium, and may be used for the preparation of that alkaloïd. (Anderson.)

2. Narcotine may be extracted directly from opium by treating that substance with ether. The solution left to evaporate deposits narcotine in the crystallised state.

*Properties.*—Narcotine crystallises in right rhombic prisms or in needles grouped in bundles, flattened, colourless, transparent and lustrous. It melts at 170° and solidifies again at 130°, in the crystalline or amorphous state, according as the cooling is slow or rapid. It is insoluble in cold *water;* boiling water dissolves $\frac{1}{7,000}$ of it. *Alcohol* and *ether* dissolve it, but not very freely. According to Duflos, it dissolves in 100 pts. cold and 20 pts. boiling alcohol of 85 per cent., in 126 pts. cold and 48 pts. boiling ether of specific gravity 0·735. The solutions are bitter and destitute of alkaline reaction. Narcotine dissolves in 2·6 pts. *chloroform* (Pettenkofer), in 60 pts. *acetic ether* (Henry), also in *oils*, both fixed and volatile.

The alcoholic or ethereal solution of narcotine deflects the plane of polarisation of a luminous ray strongly to the left; $[\alpha] = -130° 5'$ nearly. Acids modify the rotatory power considerably, altering the deviation from left to right. (Bouchardat, Ann. Ch. Phys. [3] ix. 213.)

Narcotine is not dissolved by caustic *potash* or *ammonia*. Its solutions do not produce a blue colour with *ferric salts*, a character which serves to distinguish it from morphine. (See also the reactions with Sulphuric and Nitric Acids, *infra*.)

Narcotine acts as a narcotic poison, though not so powerfully as morphine; 1·5 grm. of it is sufficient to kill a dog in a very short time.

Narcotine contains:

| *Calculated.* | | | Liebig. | Pelletier. | Regnault. | Hofmann. | Matthiessen and Foster. *Mean.* |
|---|---|---|---|---|---|---|---|
| $C^{22}$ | 264 | 63·92 | 64·09 | 63·91 | 64·25 | 64·53 | 63·79 |
| $H^{23}$ | 23 | 5·57 | 5·50 | 5·45 | 5·96 | 6·21 | 5·81 |
| N | 14 | 3·39 | 2·51 | 4·31 | 3·49 | 3·30 | 3·32 |
| $O^7$ | 112 | 27·12 | 27·90 | 26·33 | 26·30 | 25·96 | 27·08 |
| $C^{22}H^{23}NO^7$ | 413 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The composition of narcotine was first determined, to the general satisfaction of chemists, by Blyth, who in 1844 proposed the formula $C^{46}H^{25}NO^{14}$ or $C^{23}H^{25}NO^7$, supporting it by numerous analyses of the chloroplatinate, and showing at the same time that it accorded well with the most trustworthy results of previous investigations, and accounted satisfactorily for the most important transformations of narcotine, especially its resolution under the influence of oxidising agents, into opianic acid ($C^{10}H^{10}O^5$) and cotarnine (then regarded as $C^{12}H^{13}NO^3$). Accordingly Blyth's formula was for a long time regarded as expressing correctly the composition of narcotine. Wertheim, however, in 1851—founding his opinion chiefly on the composition of the volatile bases obtained by distilling narcotine with potash, some specimens, according to his observations, yielding methylamine, some ethylamine, and others tritylamine—maintained the existence of two additional varieties of narcotine homologous with that examined by Blyth, and represented respectively by the formulæ $C^{22}H^{23}NO^7$ and $C^{24}H^{27}NO^7$; while Hinterberger (Ann. Ch. Pharm. lxxxii. 312) analysed a compound of mercuric chloride with what he considered a fourth variety still homologous with the preceding, and represented by the formula $C^{21}H^{21}NO^7$. Matthiessen and Foster, on the other hand, found that six samples of narcotine prepared from different kinds of opium, Turkish, Egyptian, and Persian, yielded results agreeing very nearly with the formula above given, the difference between the highest and lowest quantities of carbon in the analyses amounting to only 0·63 per cent. Hence they conclude that there is no sufficient evidence for the existence of more than one kind of narcotine, and that it is more probable that one and the same narcotine (since when distilled with hydriodic acid, it yields 3 at. iodide of methyl, p. 27) may yield, by distillation with potash, sometimes methylamine, sometimes dimethylamine, and sometimes trimethylamine, which last appears to have been mistaken by Wertheim for its isomer, tritylamine.

*Decompositions.*—1. Narcotine becomes coloured when heated a few degrees above its melting point. At 220° it swells up, gives off ammonia, and leaves humopic acid. Heated to 200° with water in a sealed tube, it dissolves, forming a reddish very bitter liquid.

2. Strong *sulphuric acid* dissolves it, forming a yellow liquid which turns brown when heated. According to A. Husemann (Ann. Ch. Pharm. cxxviii. 305; Rép. Chim. pure, 1863, p. 284), narcotine added to cold sulphuric acid, colours it bluish-violet or yellow, which, if the liquid be gently heated, changes to orange-red, then to violet-blue at the edge of the basin, and lastly to violet-red. This reaction is very distinct, if the sulphuric acid contains 1 pt. in 2,000 of narcotine; and even if it contains only 1 pt. in 40,000, a slight carmine colour is still perceptible, passing into violet-red.—A solution of narcotine in cold sulphuric acid becomes reddish-yellow on addition of *nitric acid*. With *hypochlorite of sodium* the same colour is produced, but preceded by a carmine tint. If the solution has been heated, both reagents immediately produce a light yellow colour, becoming slightly reddish after a while.—A solution of narcotine in sulphuric acid previously heated, acquires on addition of *ferric chloride* a dark red colour, changing to cherry-red, which lasts for 24 hours (compare *Reactions of Morphine*, iii. 1052). Dilute sulphuric with the aid of heat, transforms it into a green substance, sulphonarcotide, containing the elements of neutral sulphate of narcotine *minus* 2 at. water.

3. *Chlorine gas* attacks narcotine, especially at 100°, converting it into an amorphous substance which has not been analysed.

4. In *bromine-vapour*, narcotine is coloured orange-yellow: in *iodine-vapour*, brown-

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yellow; in vapour of *chloride of iodine*, vermillion-red to yellow (Donné). The salts of narcotine are not coloured by aqueous *iodic acid*.

5. Narcotine distilled with concentrated *hydriodic acid* gives off iodide of methyl, in the proportion of 3 at. $CH^3I$ to 1 at. narcotine. (Matthiessen and Foster.)

6. According to unpublished experiments by Matthiessen and Foster, narcotine yields large quantities of chloride of methyl when heated to about 110° with strong aqueous *hydrochloric acid*. The resulting solution contains an alkaloïd which differs from narcotine in being perceptibly soluble in hot water, from which it separates on cooling as a crystalline precipitate, and by its ready solubility in solutions of the alkalis or alkaline carbonates. The composition of this product is not yet ascertained with certainty, but several analyses seem to point to the formula $C^{19}H^{17}NO^7 = C^{22}H^{23}NO^7 + 3HCl - 3CH^3Cl$.

7. Narcotine is not dissolved or decomposed by dilute *aqueous potash*, even at the boiling heat, but when boiled for some time with strong potash-ley, it forms a bitter, soluble, oily substance which appears to be the potassium-salt of a peculiar acid (*narcotic acid*). An alcoholic solution of potash dissolves narcotine in such quantity as to form a semi-solid mass. The acid contained in this potassium-salt cannot, however, be isolated; on passing carbonic acid gas into the alcoholic solution, a transparent jelly is gradually formed, which, when washed with alcohol and suspended in water, leaves crystals of narcotine. Hence narcotic acid appears to differ from narcotine only by the elements of water.

8. Narcotine heated to 200°—220° with *hydrate of potassium* or *sodium*, gives off a volatile base, which, according to the circumstances of the experiment, is either methylamine, dimethylamine, or trimethylamine. According to Hofmann (Ann. Ch. Pharm. lxxv. 367), the products vary according to the proportion of the narcotine and hydrate of potassium, an oily alkali boiling at a much higher temperature usually floating on the surface of the trimethylamine.

9. *Dilute nitric acid* dissolves narcotine at ordinary temperatures without decomposition; but on heating the solution to 50°, it deposits crystalline flocks of teropiammone, the solution retaining meconin, opianic acid, hemipinic acid, and cotarnine, the proportions of these products varying with the degree of dilution of the nitric acid. In this reaction, the opianic acid and cotarnine must be regarded as primary, the other substances as secondary products:

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^7} + O = \underset{\text{Opianic acid.}}{C^{10}H^{10}O^5} + \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^3}$$

The meconin might also be supposed to be formed by the breaking up of the narcotine, thus:

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^7} = \underset{\text{Meconin.}}{C^{10}H^{10}O^4} + \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^3}$$

or at the expense of the opianic acid:

$$\underset{\text{Opianic acid.}}{2C^{10}H^{10}O^5} = \underset{\text{Meconin.}}{C^{10}H^{10}O^4} + \underset{\text{Hemipinic acid.}}{C^{10}H^{10}O^6}$$

The hemipinic acid may also be formed by further oxidation of the opianic acid.

*Strong nitric acid* acts violently upon narcotine, giving off copious red fumes, and forming a thick red resinous matter. Gerhardt found that when narcotine is gently heated with strong nitric acid, no red vapours are evolved, but an inflammable gas, probably nitrate of methyl.

10. When a solution of narcotine in hydrochloric acid is boiled with *platinic chloride*, the narcotine is resolved into cotarnine and opianic acid, the platinic chloride being at the same time reduced to platinous chloride:

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^7} + H^2O + 2PtCl^2 = \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^3} + \underset{\text{Opianic acid.}}{C^{10}H^{10}O^5} + 2PtCl + 2HCl$$

11. The same products are formed by the action of a mixture of *peroxide of manganese and sulphuric acid* (Wöhler). On one occasion Wöhler obtained also apophyllic acid (i. 350); and by heating narcotine with peroxide of lead alone, or with peroxide of manganese and hydrochloric acid, hemipinic acid (iii. 141) was produced. A solution of sulphate of narcotine, boiled with *peroxide of lead and sulphuric acid* added drop by drop, forms narcetine or narcoteïne. (E. Marchand: see p. 25.)

12. Narcotine does not reduce *ferricyanide of potassium* in alkaline solution, and is thereby distinguished from morphine, which reduces the red to the yellow prussiate (Kieffer, Ann. Ch. Pharm. ciii. 277). When heated with absolute alcohol and iodide of ethyl, it is partially converted into hydriodate, but does not yield any substitution-product. (How, Ann. Ch. Pharm. xcii. 327.)

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SALTS OF NARCOTINE. Narcotine dissolves in acids, but the solutions have little stability, depositing the greater part of the narcotine on evaporation and often on addition of water. Many of them are soluble in alcohol and in ether. They are bitter, and redden litmus. Mixed with *tartaric acid*, and then supersaturated with an *alkaline bicarbonate*, they immediately yield a white pulverulent precipitate. *Sulphocyanate of potassium* produces in solutions of narcotine, a deep red precipitate, even if the quantity of narcotine present is extremely small; the precipitate is soluble in a slight excess of the sulphocyanate. (Oppermann, Compt. rend. xxi. 811.)

Narcotine-salts give no precipitate with *fluosilicic alcohol* (iii. 1054); with *phosphomolybdic acid*, they yield a brownish-yellow flocculent precipitate; with *phosphantimonic acid*, a white flocculent precipitate.

*Acetate of Narcotine.* Very unstable, the solution prepared in the cold, depositing narcotine when evaporated. This property may be made available for separating narcotine from morphine, the acetate of which is not decomposed by evaporation. Basic acetate of lead likewise precipitates narcotine from its solution in acetic acid.

*Chlorhydrate* or *Hydrochlorate.*—Very soluble in water. Crystallises in needles from its alcoholic solution on cooling, or from the aqueous solution evaporated to a syrup, and left for some time in a warm chamber. According to Liebig, 100 pts. narcotine absorb 9·52 pts. of dry hydrochloric acid.

When a strong acid solution of hydrochlorate of narcotine is poured into water, a semi-fluid precipitate is produced which gradually solidifies, and is soluble either in a a larger quantity of water or in hydrochloric acid. A similar precipitate is formed on gradually adding an alkali to a solution of hydrochlorate of narcotine. This precipitate contains hydrochloric acid, and is perhaps a basic hydrochlorate of narcotine. (Matthiessen and Foster.)

*Chloromercurate*, $C^{22}H^{23}NO^{7}.HCl.HgCl$ (?) White precipitate, which when dried over the water-bath, and then dissolved in a mixture of alcohol and hydrochloric acid, deposits small crystals, containing, according to Hinterberger (Ann. Ch. Pharm. lxxxii. 311), 43·64 p. c. C, 3·90 H, and 18·02 Hg. The formula above given requires 45·1 C, 4·7 H, and 17 Hg, numbers which do not agree very well with the analysis; Hinterberger assigns to the salt the formula $C^{21}H^{21}NO^{7}.HCl.HgCl$, supposing it to contain a narcotine different from ordinary narcotine (see p. 26).

*Chloroplatinate*, $C^{22}H^{23}NO^{7}.HCl.PtCl^{2}$.—Obtained by precipitating hydrochlorate of narcotine with platinic chloride, taking care not to add an excess of the latter. It separates in yellow flocks or as a yellow crystalline precipitate containing 15·80 per cent. platinum (Blyth), 15·95—15·72 (Wertheim), 15·89 (Regnault), 15·88 (How), the above formula requiring 15·99 per cent.

*Iodomercurate.*—Iodomercurate of potassium throws down from hydrochlorate of narcotine, a yellowish-white powder containing 2 at. mercury (Hg = 100) and 3 at. iodine to 1 at. narcotine. (Groves, Chem. Soc. Qu. J. xi. 97.)

*Phosphate of narcotine* is a turpentine-like mass containing crystals (Brandes).

*Sulphate.*—A solution of narcotine in dilute sulphuric acid yields by evaporation a viscid substance which gradually hardens; it dissolves in water without decomposition.

*Sulphonarcotide*, $C^{44}H^{44}N^{2}SO^{16}$ (?) is a product of the decomposition of sulphate of narcotine (p. 26). When narcotine moistened with water is heated with dilute sulphuric acid, a solution is obtained which, when more strongly heated, assumes a dark-green colour and ultimately thickens. No gas is evolved. On diluting with water and boiling, nearly the whole dissolves, and the liquid on cooling deposits an amorphous powder of a deep green colour. It appears to contain the elements of neutral sulphate of narcotine *minus* 2 at. water:

$$C^{44}H^{44}N^{2}SO^{16} = 2C^{22}H^{23}NO^{7}.H^{2}SO^{4} - 2H^{2}O$$

It gave by analysis 59·1 per cent. C, 5·3 H, and 3·6 S, the formula requiring 59·6 C, 5·0 H, and 3·6 S.

Sulphonarcotide is not attacked by *ammonia*. It dissolves in potash, forming a brown liquid from which acids reprecipitate it with green colour. Boiled with *nitric acid*, it yields sulphuric acid and a yellow substance soluble in ammonia. (Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 112.)

**NASTURAN.** Syn. with PITCHBLENDE.

**NATRIUM.** Syn. with SODIUM.

**NATROCALCITE.** Impure carbonate of calcium, occurring at Sangershausen in pseudomorphs after Gay-Lussite. Marchand (J. pr. Chem. xlvi. 95) found in these crystals 94·37 calcic carbonate, 1·15 alumina and ferric oxide, 2·02 calcic sulphate, 1·10 clay, and 1·34 water (= 99·98). A variety containing barytic sulphate has been called *neotype* by Breithaupt. Sp. gr. = 2·82—2·88.

**NATROLITE.** *Soda-mesotype. Feather zeolite.* Varieties: *Bergmannite* (*Spreustein*), *Lehuntite, Brevicite.*—This mineral forms trimetric prisms with pyramidal summits, exhibiting the combination $\infty P\,.\,P\,.\,\frac{1}{2}\,P$; also with $\bar{P}\infty$. Ratio of axes, $a : b : c = 0\cdot7165 : 1 : 1\cdot0176$. Angle $\infty P : \infty P = 91^\circ$. Cleavage perfect parallel to $\infty P$. The crystals are usually slender, often acicular, frequently interlacing, divergent, or stellate. It also occurs fibrous, radiating, and massive. Hardness = 5 to 5·5. Sp. gr. = 2·17 to 2·24. Transparent to translucent. Lustre vitreous. Colourless, grey, yellow, sometimes red or pale green. Streak white. Fracture conchoïdal. Brittle.

*Analyses: a.* From Hohentwiel in the Högau (Klaproth, *Beiträge*, v. 44).—*b.* Auvergne: crystallised (Fuchs, Schw. J. viii. 353).—*c.* Tyrol: massive, fibrous, reddish-white (Fuchs, *ibid.*).—*d.* Trezza, near Aci Castello in Sicily: white, spherical concentrically fibrous masses (S. v. Waltershausen, *Vulkanische Gesteine*, p. 269).—*e.* Brevig in South Norway: the so-called *Brevicite:* crystallised, according to G. Rose, in the form of natrolite (Scheerer, Pogg. Ann. lxv. 276; lxxxix. 26; cviii. 4, 6).—*f. Bergmannite*, from Brevig: reddish-white (Scheerer).—*g. Radiolite*, from Brevig (Scheerer).—*h. Lehuntite* from Antrim in Ireland (Thomson, *Mineralogy*, i. 338).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* |
|---|---|---|---|---|---|---|---|---|
| Silica . . . | 48·00 | 48·17 | 48·63 | 43·68 | 47·16 | 47·97 | 48·38 | 47·33 |
| Alumina .. . | 24·25 | 26·51 | 24·82 | 27·77 | 26·13 | 26·66 | 26·42 | 24·00 |
| Lime . . . | . . | 0·17 | . . | 1·73 | 0·53 | 0·68 | 0·44 | 1·52 |
| Soda . . . | 16·50 | 16·12 | 15·69 | 12·23 | 15·60 | 14·07 | 13·87 | 13·20 |
| Potash . . . | . . | . . | . . | 3·61 | . . | . . | 1·54 | . . |
| Water . . . | 9·00 | 9·13 | 9·60 | 11·27 | 9·47 | 9·77 | 9·42 | 13·60 |
| Ferric oxide . . | 1·75 | . . | 0·21 | . . | 0·53 | 0·73 | 0·24 | . . |
| Magnesia . . | . . | . . | . . | 0·29 | . . | . . | . . | . . |
| | 99·50 | 100·10 | 98·95 | 100·58 | 99·42 | 99·88 | 100·31 | 99·65 |

The analyses *a—g* may be represened by the formula $Na^2O.Al^4O^3.3SiO^2.2H^2O$, which is that of a hydrated soda-labradorite (iii. 450); if the water be regarded as basic, it may be reduced to that of an orthosilicate $(Na^2\ddot{\overline{Al}}{}^2H^4)Si^3O^{12}$. *Lehuntite* (*h*), so far as the analysis can be depended upon, appears to be the same with 1 at. water additional.

An *iron-natrolite* having the alumina partly replaced by ferric oxide, and the soda by ferrous and manganous oxides, occurs, together with brevicite, at Brevig in Norway, in dull green, opaque, prismatic crystals and semi-crystalline plates containing 46·54 per cent. silica, 18·94 alumina, 7·48 ferric oxide, 14·04 soda with a little potash, 2·40 ferrous oxide, 0·55 manganous oxide, and 9·37 water.

Natrolite occurs in cavities in amygdaloïdal trap, basalt, and other allied rocks; also in seams in granite or gneiss. It is sometimes altered to prehnite.

**NATRON.** Native carbonate of sodium, $Na^2CO^3.10H^2O$ (see CARBONATES, i. 794). *Natron* is also the German name for soda.

**NATRON-SPODUMENE.** Syn. with OLIGOCLASE.

**NAUMANNITE.** Native selenide of silver (see SILVER).

**NECTAR.** The sweet juice which collects in the nectaries or discs of various flowers. It appears to be chiefly a solution of cane-sugar and uncrystallisable sugar.

**NEEDLE-ORE.** Native sulphide of bismuth, lead, and copper (see ACICULITE, i. 37).

**NEEDLE-SPAR.** A variety of Arragonite.

**NEEDLE-STONE.** See SCOLECITE.

**NEFELINE.** Syn. with NEPHELIN (p. 30).

**NOMALITE.** Syn. with Brucite (i. 684).

**NEOCTESE.** See SCORODITE.

**NEOLITE.** A mineral occurring in mines at Arendal and Eisenach, in stellate groups of silky fibres, also massive, with green colour and silky or earthy lustre. Hardness = 1 to 2. Specific gravity = 2·77 (perfectly dried). The following analyses are by Scheerer (Pogg. Ann. lxxi. 285):

| | $SiO^2$. | $Al^4O^3$. | $Mg^2O$. | $Fe^2O$. | $Mn^2O$. | $Ca^2O$. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|---|
| 1. Arendal | 52·28 | 7·33 | 31·24 | 3·79 | 0·89 | 0·28 | 4·04 | = | 99·85 |
| 2. „ | 47·35 | 10·27 | 24·73 | 7·92 | 2·64 | . . | 6·28 | = | 99·19 |
| 3. Eisenach | 51·25 | 9·32 | 29·92 | 0·80 | . . | 1·92 | 6·50 | = | 99·71 |

The mineral may be regarded as a mixture of the isomorphous compounds $5R^2O.6SiO^2.2H^2O$ and $5R^2O.4All^2O^3.2H^2O$, the alumina and silica replacing one another in the proportion of $2All^2O^3$ to $3SiO^2$ (see iii. 433).

Neolite is a recent formation produced by the agency of infiltrating waters passing over rocks containing magnesia.

**NEOPLASE.** Native ferroso-ferric sulphate found at Fahlun in Sweden: syn. with BOTRYOGEN (i. 651).

**NEOTOKITE.** A black or brown-black amorphous mineral, occuring at Gäsböle in Finland, and apparently produced by the weathering of other minerals. Contains, according to Igelström, 35·69 per cent. silica, 25·08 ferric oxide, 24·12 manganic oxide, 0·40 alumina, 2·90 magnesia, 0·55 lime, and 10·37 water (= 99·11). When heated before the blowpipe, it gives off water, but does not fuse. (*Rammelsberg's Mineralchemie*, p. 864.)

**NEOTYPE.** A variety of natrocalcite containing baryta (p. 28).

**NEPHELIN.** *Sommite, Cavolinite, Beudanite.—Elæolite, Fettstein, Pierre grasse.* A silicate occurring in prisms belonging to the hexagonal system, and exhibiting the combination ∞P . oP . P (fig. 240, ii. 139), mostly however without P; occasionally also with the faces ∞P2, ∞P$\frac{3}{2}$, and others. For P, the length of the vertical axis is 0·8376. Angle P : P in the terminal edges = 139° 19′; in the lateral edges = 88° 6′. Cleavage imperfect parallel to oP and ∞P. Also massive, compact, and thin columnar.

Hardness = 5·5 to 6. Specific gravity 2·5 to 2·64. Lustre vitreous to greasy. Colourless, white, or yellowish; the massive varieties also dark green, greenish or bluish-grey, brownish and brick-red. Transparent to opaque. Fracture subconchoïdal. Brittle.

The name *nephelin* includes the colourless crystallised varieties; *elæolite*, the coarse massive varieties, with a greasy lustre.

Before the blow-pipe, nephelin melts with difficulty to a vesicular glass; elæolite easily. Both dissolve slowly in borax, and give with cobalt-solution a greyish-blue colour on the fused edge. Both gelatinise easily in acids.

*Analyses.*—1. Of Nephelin. *a.* From Vesuvius (Scheerer, Pogg. Ann. xlvi. 291; xlix. 359).—*b.* From the dolerite of the Katzenbuckel in the Odenwald (Scheerer, *loc. cit.*).—*c.* From Löban in the Lausitz (Heidepriem, J. pr. Chem. l. 500).

2. Of Elæolite.—*a.* From Fredriksvärn in Norway (Scheerer, *loc. cit.*).—*b.* Brevig in Norway (Scheerer).—*c.* Miask in the Ural (Scheerer).—*d.* Magnet Cove, Arkansas (Smith and Brush, Sill. Am. J. [2] xvi. 365):

| | *Nephelin.* | | | *Elæolite.* | | | | |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *a.* | | *b.* | *c.* | *d.* |
| | | | | Green. | Brown. | Brown. | White. | Flesh-red. |
| Silica | 44·04 | 43·70 | 43·50 | 45·23 | 45·53 | 44·46 | 44·18 | 44·46 |
| Alumina | 34·06 | 32·31 | 32·33 | 32·66 | 32·06 | 31·84 | 33·18 | 30·97 |
| Ferric oxide | 0·44 | 1·07 | 1·42 | 0·56 | 1·41 | 1·11 | 0·69 | 2·09 |
| Soda | 15·91 | 15·83 | 14·13 | 15·71 | 15·97 | 15·71 | 15·86 | 15·61 |
| Potash | 4·52 | 5·60 | 5·03 | 5·66 | 4·76 | 5·17 | 5·75 | 5·91 |
| Lime | 2·01 | 0·84 | 3·55 | 0·33 | 0·40 | 0·28 | 0·29 | 0·66 |
| Magnesia | . . | . . | 0·11 | . . | . . | . . | 0·07 | . . |
| Water | 0·21 | 1·39 | 0·32 | 0·61 | 0·78 | 2·07 | 0·45 | 0·95 |
| | 101·19 | 100·74 | 100·39 | 100·76 | 100·91 | 100·64 | 100·47 | 100·65 |

Scheerer found also a trace of sulphuric acid in nephelin; Bromeis found a trace of chlorine.

The preceding analyses lead to the formula $4M^2O.3SiO^2 + 2(2Al^4O^3.3SiO^2) = \overset{''''}{Si}\overset{''''''}{All}{}^8\overset{'}{M}{}^8O^{24}$, or, as most of the analyses give 1 atom potash to 3 atoms soda, $\overset{''''}{Si}{}^9\overset{''''''}{All}{}^2(\frac{1}{4}K.\frac{3}{4}Na)^8O^{24}$. The quantity of lime is variable and insignificant.

Nephelin occurs in crystals in the older lavas of Vesuvius, with mica, idocrase, &c.; also at Cape di Bove near Rome, and the other localities above mentioned. Elæolite is found imbedded in the zircon-syenite of Brevig, Stavern, and Fredericksvärn in Norway; also with felspar, mica, zircon, pyrochlore, &c., in the Ilmen mountains in Siberia; also at Litchfield, in the State of Maine, with cancrinite; and in the Ozark mountains, Arkansas, with brookite and schorlemite.

Nephelin and elæolite easily undergo alteration, producing zeolites, such as Bergmannite or Thomsonite; the large amount of soda in these minerals fits them especially for this mode of transformation.

*Gieseckite*, a mineral occurring in greenish-grey six-sided prisms having a greasy lustre, has been shown by Blum to be a pseudomorph after this species, differing from it merely in containing 4·88 per cent. water. Blum also considers *liebenerite* (iii. 589) as a similar pseudomorph. Elæolite has been observed altered to mica.

**NEPHRITE.** *Jade* in part, *Beilstein*.—A hard, compact, light green, bluish, or whitish stone, translucent, tough, breaking with a splintery fracture and glistening surface. Hardness = 6—7. Specific gravity = 2·9—3·1. It belongs to the hornblende family, but varies in composition, and is not a distinct mineral species.

*Analyses: a, b, c.* From the East: *a.* Kastner (Gehlen's J. ii. 459).—*b.* Schafhäutl, Ann. Ch. Pharm. xlvi. 338).—*c.* Rammelsberg (Pogg. Ann. lxii. 148).—*d.* Damour, Ann. Ch. Phys. [3] xvi. 469).—*e.* Scheerer (Pogg. Ann. lxxxiv. 379).—*f.* From New Zealand: *Punama stone;* green (Scheerer, *loc. cit.*):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|
| Silica | 50·50 | 58·88 | 54·68 | 58·24 | 57·38 | 57·10 |
| Alumina | 10·00 | 1·56 | . . | . . | 0·68 | 0·72 |
| Ferrous oxide | 5·05 | 2·53 | 2·15 | 1·14 | 1·35 | 3·39 |
| Manganous oxide | . . . | 0·80 | 1·39 | | | |
| Magnesia | 31·00 | 22·39 | 26·01 | 27·14 | 25·88 | 23·29 |
| Lime | . . . | 12·51 | 16·06 | 11·94 | 12·20 | 13·48 |
| Potash | . . . | 0·80 | | | | |
| Water | 2·75 | 0·27 | 0·68 | . . | 2·55 | 2·50 |
| Chromic oxide | 0·05 | | | | | |
| | 99·35 | 99·74 | 100·97 | 98·46 | 100·04 | 100·48 |

If the first analysis be left out of consideration, nephrite appears to have nearly the composition of tremolite (see HORNBLENDE, iii. 169).

Nephrite occurs in connection with talcose rock or slate and granular limestone. In China, New Zealand and North-west America, it is worked into images and ornaments. The name is from νεφρός a kidney, the stone having been formerly supposed to be a cure for diseases of the kidney.

**NEROLI, OIL or ESSENCE OF.** *Oil of Orange-flowers.*—A volatile oil obtained by distilling orange-flowers with water. It is nearly colourless when fresh, but soon turns red on exposure to light. According to Soubeiran and Capitaine (J. Pharm. xvii. 619), it is composed of two distinct oils, one of which has a very fragrant odour, and dissolves abundantly in the orange-flower water which passes over in the distillation, while the other is nearly insoluble in water, and occurs only in the oily portion of the distillate. The first-mentioned oil is reddened by sulphuric acid, and communicates this property to the entire essence. According to Döbereiner, oil of neroli produces a peculiar acid by contact with platinum-black. Nitric acid colours the oil brown.

*Neroli-camphor.* According to Boullay (J. Pharm. xiv. 496) and Plisson (*ibid.* xv. 152, xx. 63), oil of neroli mixed with alcohol of 90 per cent. deposits a solid substance melting at 50°, insoluble in water, sparingly soluble in boiling absolute alcohol, very soluble in ether. Boullay and Plisson found in it 83·76 per cent. carbon, 15·09 hydrogen, and 1·15 oxygen; it is probably a hydrocarbon.—For further details respecting the oil and camphor, see *Gmelin's Handbook*, xiv. 386–388.

**NERVOUS TISSUE.** (Vauquelin, Ann. du mus. d'hist. nat. 1811, p. 212.—Couerbe, Ann. Ch. Phys. [2] lvi. 164.—Frémy, *ibid.* [3] ii. 463.—Lassaigne, J. Chim. méd. [2] i. 344.—V. Bibra, *Untersuchungen über das Gehirn des Menschen und der Wirbelthiere.*—W. Müller, *Die chem. Bestandth. des Gehirns.*—Breed, Ann. Ch. Pharm. lxxxiii. p. 124.)

The nervous system of the higher animals is composed, for the most part, of nerve-fibres and nerve-cells or nerve-vesicles, the former being found in the nerves, and in the "white matter" of the brain and spinal cord, the latter in the "grey matter" of the same, in the ganglia, and in some of the peripheral organs of sense. The peculiar "electric organs" of certain fishes must be considered as part of the nervous system (see ELECTRICITY, ii. 476). The nerve-fibre consists of—1. A "sheath," probably analogous in nature to elastic tissue.—2. A hollow cylinder or "medullary substance," a mixture of some form of albumin with various fatty bodies, having a homogeneous appearance during life, and undergoing a kind of coagulation after death.—3. A central stem or "axis-cylinder," composed of some protein-compound or compounds with little or no fat, thought by many to be fluid during life and to coagulate spontaneously at death. There are also other "gelatinous" fibres having a different structure. The typical nerve-vesicle consists of:—1. An envelope probably continuous and identical in nature with the nerve-sheath.—2. A nucleus (with nucleolus).—3. "Contents," probably composed of some protein-substance with fatty and other granules. The vesicles or cells vary, however, exceedingly in form, size, &c.

The reaction of living nerve is during inaction, neutral (amphichromatic); during strong action, acid; the reaction of dead nerve is acid (Funke, Arch. Anat. Phys. 1859, p. 835). Du Bois-Reymond found the electric organs of *Malapterurus* neutral immediately after death, but becoming acid on the third day (*ibid.* p. 847). Nerve-substance, unlike muscle-substance, becomes acid when boiled.

The specific gravity of the "white matter" is 1·041, of the "grey" 1·034.

Frémy represents 100 pts. of cerebral substance as consisting of 80 water, 5 fat, 7 albumin, and 8 extractives and salts. v. Bibra gives 75·6 per cent. water, and from 12 to 16 per cent. fat. The "white matter" contains less water than the "grey," the mean of the former being 73 per cent., of the latter 85 per cent. The "white" is richest in fat, possessing 14·8 per cent., while the "grey" has only 4·7 per cent. (Lassaigne). According to v. Bibra, the spinal cord contains less water and more fat than the brain, viz. 66 per cent. of water and 25 per cent. of fat, while the nerves again have less water and more fat than the spinal cord, though the quantities seem to vary excessively. Schlossberger (Müller's Arch. 1858, p. 309) gives the brain of foetus as containing from 87·9 to 92·6 per cent. of water and from 1·6 to 3·7 per cent. of fat, results very closely agreeing with those of v. Bibra.

In 100 pts. of fresh brain, Breed found 0·027 ash, in 100 pts. of which were:—

| | | | |
|---|---|---|---|
| Phosphate of Potassium | 55·24 | Chloride of Sodium | 4·74 |
| " " Sodium | 22·93 | Sulphate of Potassium | 1·64 |
| " " Iron | 1·23 | Phosphoric acid (free) | 9·15 |
| " " Calcium | 1·62 | Silicic acid | ·42 |
| " " Magnesium | 3·40 | | |

No department of physiological chemistry has been so little studied, or studied with so little profit, as that of the nervous tissue. Exact knowledge concerning the protein-compounds in it is wholly wanting. The substance forming the axis-cylinder seems to belong to the same series as fibrin and syntonin (myosin); it differs from the former by its insolubility in a solution of nitre, from the latter by its insolubility in dilute acids. The protein constituent of the medullary substance and of the cell-contents seems to be some form of soluble albumin. It has been thought to be casein. Our acquaintance with the peculiar fatty bodies is also very unsatisfactory. Besides cholesterin, which occurs to the extent of 20 per cent. of total fat (v. Bibra), olein, stearin, and palmitin, there have been obtained various bodies whose nature is much disputed. (See Cerebrote, Cephalote, Myelin, Stearoconote, Cerebrin, Cerebric Acid, Oleophosphoric Acid, Glycerophosphoric Acid, Lecithin.)

W. Müller found in human brain a small quantity of creatine, 0·05 grm. in 4 pounds; in ox-brain he found no creatine, but a body resembling leucine, together with uric acid and xanthine or hypoxanthine. He also found in the same brain a very considerable quantity of inosite, 20 grms. in 50 pounds. Both v. Bibra and W. Müller found lactic acid, the latter obtaining 12 grms. from 50 pounds. Lorenz (Henle.-Meissner, 1859, p. 290) found no creatine, leucine, inosite, or lactic acid; he obtained, however, both xanthine and hypoxanthine. Herz (*ibid.* 1860, p. 311) corroborates Müller. M. Schultze found urea and creatinine in the electric organs of the torpedo. Formic and acetic acid are said to be obtained by distillation of the watery extract of brain. The presence of the above crystalline bodies indicates a metamorphosis, very similar to that which probably takes place in muscles; but we know nothing of the various steps. The large amount of phosphorus in nervous tissue (1·388—1·79 per cent. of dry brain-substance according to Borsarelli) has prompted many to attribute much to that particular element. Mental effort is said to increase the phosphates of the urine; but whether directly or indirectly is uncertain.

Neukomm (Arch. Anat. Phys. 1860, p. 1) found in human brain in various diseases, leucine, creatine, and inosite, the latter at times in very notable quantities. Tyrosine was invariably absent. Grohe (Med. Centr. 1864, p. 870) found glycogen (without sugar) in the brain of a diabetic. M. F.

**NEUROLITE.** A fibrous mineral from Stamstead in Lower Canada, containing, according to Thomson, 73·00 per cent. silica, 17·35 alumina, 3·25 lime, 1·5 magnesia, and 4·3 water.

**NEWJANSKITE.** Syn. with Iridosmine (iii. 324).

**NEWKIRKITE.** Manganic hydrate (iii. 810) from Neukirchen in Alsace, where it forms a coating on red hæmatite.

**NICENE.** See Chloronicric Acid (i. 921).

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**NICKEL.** *Symbols* and *Atomic Weights*, Ni = 29·37; Nni' = 58·74.

This metal is closely allied to iron and cobalt, and is associated with them in meteorites as well as in most of its terrestrial ores. The principal ore of nickel is the proto-arsenide, Nni''As, a copper coloured mineral, to which the German miners, having in vain attempted to extract copper from it, gave the name of *kupfer-nickel*, or false copper. This mineral was found by Cronstedt, in 1751, to contain a peculiar metal which he called nickel.

Nickel also occurs as diarsenide (*white nickel pyrites* or *cloanthite*); arsenate (*nickel-bloom* or *annabergite*); antimonide (*breithauptite*); arsenio-sulphide (*gersdorffite* or *nickel-glance*); antimonio-sulphide (*ullmanite*); as oxide, sulphide (*capillary pyrites* or *millerite*), sulphide of nickel and bismuth (*grunauite*), sulphide of nickel and iron; carbonate (*emerald-nickel*), sulphate (*pyromelin*) and silicate (*pimelite*).

*Preparation.*—Principally from copper-nickel and from *speiss*. Speiss is a deposit formed in the pots in which roasted arsenide of cobalt mixed with copper-nickel is fused with carbonate of potassium and pounded quartz, for the preparation of smalt in the blue-colour works; it collects below the blue glass in the form of a metallic alloy, the nickel not oxidising so easily in roasting as the cobalt. It contains, besides nickel, principally iron, cobalt, manganese, bismuth, antimony, arsenic, and sulphur. The following are some analyses of speiss: *a.* of unknown origin (Berthier); *b.* from Bohemia (Anthon, J. pr. Chem. ix. 12); *c.* from Henninger's German-silver works; this sample has been previously purified; its structure was coarsely laminar. (Francis, Pogg. Ann. l. 519.)

| | Ni. | Co. | Fe. | Cu. | Bi. | Sb. | As. | S. | Sand. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *a.* | 49·0 | 3·2 | . . | 1·6 | . . | trace | 37·8 | 7·3 | 0·6 | = | 100·0 |
| *b.* | 36·2 | 1·3 | 1·1 | 1·5 | 21·5 | . . | 29·9 | 6·9 | . . | = | 98·4 |
| *c.* | 52·6 | 3·3 | 10·1 | . . | . . | . . | 34·1 | 1·0 | . . | = | 101 |

The copper-nickel or the speiss is generally roasted in a state of powder (at a gentle heat at first, to prevent it from baking together), whereby the greater part of the arsenic is removed, the nickel oxidated, and a saving of nitric acid thus effected in the subsequent treatment. Since, however, the roasting process leaves a portion of the arsenic combined with the nickel in the form of arsenic acid, the roasted ore must be several times intimately mixed with charcoal dust and again roasted, as long as vapours of arsenic continue to be evolved. Erdmann moistens the roasted speiss with water and places it in a cellar for some time, whereby it is rendered more easily soluble.

The further separation of the arsenic and other metals may be effected by one of the following processes:

1. Laugier dissolves the roasted copper-nickel or the speiss in nitric acid, passes sulphuretted hydrogen through the dilute acid solution till all the arsenic, copper, bismuth, and antimony are precipitated; then filters; precipitates all the iron, cobalt, and nickel with carbonate of sodium; washes the precipitate thoroughly, and treats it first with oxalic acid and then with ammonia, as described with reference to the preparation of cobalt (i. 1040), repeating the solution of the nickel-oxalate in aqueous ammonia, till the liquid which stands above the resulting precipitate no longer exhibits a rose-colour, and is almost wholly free from cobalt.

2. Berthier dissolves roasted speiss or roasted copper-nickel—together with the quantity of iron found by previous experiments to be necessary for the separation of the arsenic acid—in boiling nitromuriatic acid containing excess of nitric acid; evaporates the solution to dryness; treats the residue with water, which leaves a large quantity of ferric arsenate undissolved: and adds carbonate of sodium to the filtrate, stirring all the while, till the precipitate begins to exhibit a green tint: the whole of the ferric arsenate is thereby thrown down, together with part of the cupric oxide. If the precipitate, which is white at first, does not ultimately turn brown, it is a sign that the quantity of ferric oxide present is not sufficient to carry down the arsenic acid with it; consequently, more ferric chloride must be added, and the ferric oxide again cautiously precipitated by carbonate of sodium. The filtrate is next treated with sulphydric acid to precipitate the rest of the copper; the liquid filtered from the sulphide of copper is completely precipitated at a boiling heat by carbonate of sodium; the precipitate, consisting of the carbonates of nickel and cobalt, thoroughly washed and diffused in water; chlorine gas passed through the liquid as long as it is absorbed; the solution exposed to the air to allow the excess of chlorine to evaporate, and then filtered. The filtrate contains chloride of nickel free from cobalt; it may be precipitated by an alkali.

3. Roasted speiss is digested in hydrochloric acid, which leaves nothing undissolved but 3 or 4 per cent. of sulphur, and a few granules which have retained their metallic

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state; the liquid is diluted with water, and separated by filtration from the precipitated oxychloride of bismuth; the filtrate heated to the boiling point; aqueous ferric chloride added to it, and then milk of lime in small portions—the boiling being still continued—till a filtered sample exhibits no longer a pale green, but bluish-green colour, and gives with potash a precipitate, which, when heated on charcoal before the blowpipe, yields an infusible mass of spongy nickel. As long as the reduced nickel continues fusible, arsenic is present, and further addition of lime is necessary; it is best to add the lime in slight excess, in order to insure the complete separation of the arsenic. The liquid is then filtered, and the nickel precipitated by milk of lime free from iron. (Erdmann.)

4. Unroasted speiss is fused with sulphur and carbonate of potassium, as described for the preparation of cobalt (i. 1040, 4); and the resulting sulphide of nickel (which appears free from arsenic after one such fusion and subsequent washing with water) is dissolved in nitric acid or a mixture of nitric and sulphuric acids, and subjected to further treatment for the separation of bismuth, copper and cobalt, as described under Cobalt. (Wöhler, Pogg. Ann. vi. 227.)

5. Thomson (Ann. Phil. xiv. 144) digests pounded speiss in dilute sulphuric acid, frequently adding nitric acid as long as any action is thereby produced; then decants the green solution from the arsenious acid which separates; and after evaporation and cooling, adds to the solution either sulphate of potassium, or a quantity of carbonate equal to half the weight of the speiss. The liquid, after concentration and repose, deposits crystals of niccolo-potassic sulphate, which may be further purified by a second crystallisation.

6. Cloez (Jahresb. 1857, p. 619) dissolves finely pulverised and perfectly roasted copper-nickel in strong hydrochloric acid; mixes the solution with excess of acid sulphite of sodium; and boils till the arsenic acid is completely reduced to arsenious acid, and the excess of sulphurous acid is driven off; then passes sulphydric acid gas through the lukewarm liquid to precipitate arsenic, copper, antimony, lead and bismuth; filters the saturated liquid after twelve hours' standing; evaporates the filtrate; treats the residue with water; precipitates iron and cobalt from the filtrate by carbonate of barium or calcium, after treating it with chlorine; and removes the dissolved baryta or lime with sulphuric acid. The filtered liquid then yields with carbonate of sodium a precipitate of pure carbonate of nickel, which may be ignited and reduced. The solution of speiss in nitro-muriatic acid may be treated in the same manner, after the nitric acid has been expelled by boiling with excess of hydrochloric acid.

7. The following method is adopted in a manufactory at Birmingham for separating nickel and cobalt from the Hungarian speiss, containing 6 per cent. of nickel and 3 per cent. of cobalt. The ore is first fused with chalk and fluorspar, the slag thrown away, and the fused product is ground to powder, and roasted for 12 hours in a reverberatory furnace, till no more fumes of arsenious acid are given off. The roasted product then dissolves almost completely in hydrochloric acid. The solution is diluted with water, mixed with chloride of lime to convert the iron into sesquioxide, and with milk of lime to precipitate that oxide together with the arsenic. The precipitate (which is of no further use) is then washed, and sulphuretted hydrogen passed through the clear liquid till a filtered sample gives a black precipitate on the addition of ammonia. The precipitated sulphides (which are likewise of no further use) having been washed with water, the solution is next treated with chloride of lime to precipitate the cobalt, and then with milk of lime to throw down the nickel. The cobalt-precipitate is converted either into sesquioxide by gentle ignition, or into protoxide by strong ignition, and sent into the market in one or other of these forms: it is said to be very pure. The precipitated nickel is reduced by charcoal, and sold to the manufacturers of German silver. (Louyet, J. Pharm. [3] xv. 204.)

8. At Klefva in Sweden, a magnetic pyrites containing copper and nickel is worked for the extraction of the latter metal. The ore after being roasted in heaps is fused in a shaft-furnace, with addition of quartz. The greater part of the iron then passes into the slag, as silicate, in the treatment of copper-ores (ii. 24), and a matt is obtained containing about 6 per cent. nickel, together with copper, iron, and sometimes a little sulphur. This matt is reduced to coarse powder and roasted in a reverberatory furnace, then fused again in a shaft-furnace. After a certain number of alternate fusions and calcinations thus conducted, matts are obtained very rich in nickel, the final product being an alloy formed of 70—80 per cent. nickel, 18—22 copper, and 1·5 to 2·5 iron. This alloy is broken up into small pieces and sent into the market as "crystallised nickel." (Pelouze et Frémy, *Traité*, 3me. ed. iii. 530.)

For other modes of preparation see the work just cited; also *Gmelin's Handbook*, v. 355-360.

In all processes for obtaining a pure salt of nickel, the most difficult point is the separation of the cobalt. The methods of separating these two metals have been already described under COBALT (i. 1046); the best and easiest of execution is perhaps that of A. Stromeyer founded on the precipitation of cobalt by nitrite of potassium. Good results are also obtained by Liebig's method with cyanide of potassium and mercuric oxide (see further p. 39), and by that of H. Rose with chlorine and carbonate of barium, as in the sixth mode of preparation above described, which yields a perfectly pure salt of nickel.

*Reduction.*—A pure solution of nickel having been obtained by one of the processes above described, it is precipitated by a caustic alkali or alkaline carbonate; the bulky precipitate of hydrate or carbonate of nickel is carefully washed; then spread out on filters to dry, and the desiccation is finished by heat. The dried precipitate is then introduced, either alone or made up into a stiff paste with oil, into a crucible lined with charcoal, and exposed to the heat of a powerful air- or blast-furnace, whereby the metal is obtained in the form of a fused mass. On the large scale the reduction is effected by a cementation process. A number of cylinders of refractory clay are set vertically in a furnace so that the flame may play round them on all sides. They are open at top and terminate below in truncated cones, the bases of which are below the fire-bars, and are provided with apertures for removing the charge. The dried oxide of nickel, in lumps or small cubes measuring about 0·02 mm. in the side, is mixed with pulverised charcoal and thrown in at the top of the cylinder, and the fire is strongly urged. The oxide of nickel is then decomposed by the heated carbonic oxide in the furnace, the reduced metal retaining the form of the lumps or cubes of oxide introduced. The reduced metal is discharged from time to time through the orifices in the bottoms of the cylinders, a fresh charge being at the same time introduced by the top, so that the process is to a certain extent continuous. To obtain the metal in ingots, the lumps formed as above are fused at the strongest heat of a forge-fire.

Metallic nickel may also be obtained by igniting the oxide in hydrogen gas, or by heating oxalate of nickel or of nickel-ammonium under a layer of pounded glass not containing any heavy metal. These processes yield it in the pulverulent form.

Nickel may be obtained in brilliant white laminæ by the electrolysis of an ammoniacal solution of sulphate of nickel and ammonium. (A. C. and E. Becquerel, Compt. rend. lv. 18.)

The nickel of commerce is seldom pure. Lassaigne found the composition of three samples from different sources to be as follows:

| | Ni. | Co. | Cu. | Fe. | As. | $Al^2O^3$. | Silicious residue. | | |
|---|---|---|---|---|---|---|---|---|---|
| German . . | 66·75 | . . | 27·50 | 12·55 | . . | . . | 3·70 | = | 100 |
| " . . | 54·60 | . . | 30·10 | 11·30 | trace | . . | 4·00 | = | 100 |
| English . . | 73·30 | 22·10 | trace | 1·00 | . . | 2·50 | 0·50 | = | 100 |

L. Thompson (London Journal of Arts, Feb. 1863, p. 65) found in various samples of commercial nickel from 76 to 86 per cent. of the pure metal. He obtained a purer product containing 88 per cent. nickel by roasting nickel-glance (arsenio-sulphide of nickel) with half its weight of quicklime in a cupola-furnace urged by a blast.

*Properties.*—Pure nickel in the compact state is silver-white, ductile, malleable, not much more fusible than iron, which, according to Deville, it even surpasses in tenacity. Nickel containing small quantities of carbon is more fusible than the pure metal. The specific gravity of nickel is 8·279, increasing to 8·666 by forging. Nickel is magnetic at ordinary temperatures, but loses this power at 250°, recovering it however on cooling. Nickel previously heated burns in *oxygen gas* like iron, and is converted into oxide. The pulverulent metal obtained by reduction in hydrogen at a low red heat, takes fire spontaneously in contact with the air. Nickel dissolves in ***hydrochloric acid*** and in dilute ***sulphuric acid*** with evolution of hydrogen, easily in ***nitric*** and in ***nitromuriatic acid.***

**NICKEL, ALLOYS OF.** Nickel unites with other metals, forming for the most part white malleable alloys (see the several metals). The most important is the alloy of nickel, copper and zinc, known as German silver (see COPPER, ALLOYS OF, ii. 51). Meteoric iron is an alloy of iron and nickel (see METEORITES, iii. 377). An alloy of nickel and *aluminium*, $Al^6Ni$, is obtained in large tin-white laminæ, of sp. gr. 3·647, by melting 8 pts. aluminium with 3 pts. sublimed chloride of nickel and 20 pts. chloride of potassium and sodium, and treating the resulting regulus with dilute hydrochloric acid Michel, Ann. Ch. Pharm. cxv. 102). The alloys of nickel with arsenic and antimony occur as natural minerals.

**NICKEL, ANTIMONIDE OF.** *Antimonial Nickel, Breithauptite.* $Ni^2Sb$ or $Nni''Sb$.—This mineral was formerly found in the Andreasberg mountains, but has long been exhausted; it occurred in thin hexagonal plates, also massive and disseminated, with metallic lustre, light copper-red colour on the fresh fracture; sp. gr. 7·541; hardness 5·5.

**NICKEL, ANTIMONIO-SULPHIDE OF.** See NICKEL-GLANCE (p. 43).

**NICKEL, ARSENATE OF.** *Annabergite*, *Nickel-bloom*, *Nickel-green*, $Ni^3AsO^4.4H^2O$ or $Nn''i^3As^2O^8.8H^2O$.—This compound occurs native in soft, apple-green, capillary, monoclinic crystals, also massive and disseminated. Hardness = 2·5 to 3·0. Sp. gr. = 3·078—3·131. The following analyses are—*a*. by Berthier (Ann. Ch. Phys. [2] xiii. 5 ; *b*. by Stromeyer (Schw. J. xxv. 220); *c*. by Kersten (Pogg. Ann. x. 251):

| | $As^2O^3$. | $Ni^2O$. | $Co^2O$. | $H^2O$. | | | |
|---|---|---|---|---|---|---|---|
| *a*. *Allemont* | 36·8 | 36·2 | 2·5 | 25·5 | | = | 101 |
| *b*. *Riechelsdorf* | 36·97 | 37·85 | . . | 24·32 | $Fe^4O^3$ 1·13, $SO^3$ 0·23 | = | 100 |
| *c*. *Schneeberg* | 38·30 | 36·20 | 1·53 | 23·91 | $Fe^2O$ trace | = | 99·94 |

The formula requires 38·41 $As^2O^3$, 37·52 $Ni^2O$ and 24·0 $H^2O$. The mineral occurs on white nickel, at Allemont in Dauphiny, and is supposed to result from a decomposition of this ore; it is found also at Kamsdorf near Saalfeld, at Annaberg, and in other mines of nickel ores. It has occasionally been observed associated with copper-nickel, in the cobalt mine at Chatham, Connecticut (Dana, ii. 418). Respecting the artificial arsenate of nickel, see i. 313.

**NICKEL, ARSENIDES OF.** A very small quantity of arsenic is sufficient to render nickel fusible before the blowpipe under borax. (Berzelius.)

*α*. $Ni^4As$ or $Nni^2As$. A brittle non-magnetic alloy having this composition, is obtained by heating 100 pts. of finely divided nickel in a close vessel with excess (200 pts.) of arsenic, or by heating arsenate of nickel to whiteness in a charcoal-lined crucible. L. Gmelin (*Handbook*, v. 388) describes, on the authority of Plattner, an arsenide of nickel called *Placodin*, having nearly the same composition, viz. 57·05 per cent. nickel, 39·71 arsenic, 0·92 cobalt, 0·86 copper, a trace of iron, and 0·62 sulphur.

*β*. $Ni^3As$ or $Nni^3As^2$. Speiss is sometimes found in crystals of the dimetric system having this composition. A specimen from a disused smalt-furnace was found by Wöhler (Pogg. Ann. xxv. 302) to contain 52·70 per cent. nickel, 44·05 arsenic, 1·65 sulphur, and 1·60 manganese, iron, and copper, the formula $Ni^3As$ requiring 54·13 nickel and 45·87 arsenic. This crystallised speiss, which is sometimes found in the speiss run out from the crucibles, appears to be produced by long continued fusion of copper-nickel contained in cobalt ores.

*γ*. $Ni^2As$ or $NniAs$. This is the composition of *Copper-nickel*, the principal ore of the metal, which occurs in hexagonal prisms, oP . ∞P, isomorphous with antimonial nickel, having the length of the principal axis = 0·81944, more frequently massive, with nearly impalpable structure; also reniform with columnar structure; also reticulated and arborescent. Hardness = 5·5. Sp. gr. = 7·33—7·671. Opaque, with metallic lustre and copper-red colour, with a grey to blackish tarnish. Streak pale brownish-black. Fracture uneven. Brittle. Before the blowpipe on charcoal, it emits arsenical fumes, and melts to a white globule, which darkens on exposure to the air. In nitric acid it becomes covered with a green coating and dissolves in nitro-muriatic acid.

*Analyses.*—*a*. From Riechelsdorf (Stromeyer, Gött. gel. Anz. 1817, p. 204).—*b*. From Krägeröe in Norway: sp. gr. 7·662 (Scheerer, Pogg. Ann. lxv. 292).—*c*. From Ayer: sp. gr. 7·39 (Ehelmen, Ann. Min. [4] xi. 55).—*d*. Westphalia (Schnabel, *Rammelsberg's Mineralchemie*, p. 20).—*e*. Allemont in Dauphiny (Berthier, Ann. Ch. Phys. [2] xiii. 52).—*f*. From Balen in the Pyrenees (Berthier, *loc. cit.*):

| | As. | Sb. | S. | Ni. | Fe. | Pb. | Co. | Cu. | Gangue. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *a*. | 54·73 | . . | 0·40 | 44·21 | 0·34 | 0·32 | . . | . . | . . | = | 100 |
| *b*. | 54·35 | . . | 0·14 | 44·98 | 0·21 | . . | . . | 0·16 | . . | = | 99·84 |
| *c*. | 52·71 | . . | 0·48 | 45·37 | . . | . . | . . | 1·44 | . . | = | 100 |
| *d*. | 54·05 | 0·05 | 2·18 | 43·50 | 0·45 | . . | 0·32 | . . | 0·20 | = | 100·75 |
| *e*. | 48·80 | 8·00 | 2·00 | 39·94 | . . | . . | 0·16 | . . | . . | = | 98·90 |
| *f*. | 33·0 | 27·8 | 2·8 | 33·0 | 1·4 | . . | . . | . . | 2·0 | = | 100 |

Copper-nickel is found accompanying cobalt, silver and copper, in the Saxon mines of Annaberg, Schneeberg, &c.; also in Thuringia, Hesse and Styria, and at the other localities above-mentioned; occasionally also in Cornwall, and at Leadhills in Scotland. At Chatham, Connecticut, it is found in gneiss, associated with arsenide of cobalt.

*δ*. $NiAs$ or $NniAs^2$. This compound occurs in two forms:—1. As *Cloanthite* or *White Nickel*, in monometric forms, viz. cubes, octahedrons, trapezohedrons, 2O2, and the combinations shown in figures 174, 175, 176, 202, 205, &c. (ii. pp. 123, 124, 130), isomorphous with smaltin, $CcoAs^2$ (i. 1040).—2. As *Rammelsbergite*, in trimetric prisms having the angle ∞P : ∞P = 123°—124°. Also massive and in reticulated and imitative shapes. Hardness = 5·25 to 6. Specific gravity = 6·466—7·2. Lustre metallic. Colour tin-white, inclining when massive to steel-grey. Streak greyish

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black. Opaque. Fracture granular and uneven. Brittle; Rammelsbergite, however, is slightly ductile. Behaves before the blowpipe like copper-nickel.

*Analyses.*—*a.* From Schneeberg (Hofmann. Pogg. Ann. xxv. 491, 494).—*b.* Riechelsdorf (Booth, *ibid.* xxxii. 395).—*c.* Joachimsthal in Bohemia: specific gravity 6·89 (Marian, *Rammelsberg's Mineralchemie*, p. 21).—*d.* Kamsdorf near Saalfeld: specific gravity 6·735 (Rammelsberg, *ibid.*).—*e.* The Annivierthal in the Valais (Berthier, Ann. Min. [3] xi. 504).—*f.* Allemont (Rammelsberg, *loc. cit.*).—*g.* Chatham, Connecticut; *Chathamite;* massive (Shepard, Sill. Am. J. xlvii. 351).

| | As. | S. | Ni. | Co. | Fe. | Cu. | Bi. | |
|---|---|---|---|---|---|---|---|---|
| *a.* | 71·30 | 0·14 | 28·14 | . . | . . | 0·50 | 2·19 | = 102·27 |
| *b.* | 72·64 | . . | 20·74 | 3·37 | 3·25 | . . | . . | = 100 |
| *c.* | 71·47 | 0·58 | 21·18 | 3·62 | 2·83 | 0·29 | . . | = 99·97 |
| *d.* | 70·34 | . . | 28·40 | . . | . . | . . | . . | = 98·74 |
| *e.* | 65·02 | 2·90 | 26·75 | 3·93 | 1·40 | . . | . . | = 100 |
| *f.* | 71·11 | 2·29 | 18·71 | . . | 6·82 | . . | . . | = 98·93 |
| *g.* | 70·00 | . . | 12·16 | 1·35 | 17·70 | . . | . . | = 101·21 |

Cloanthite occurs with silver and copper in the same localities as smaltin (ii. 1040); the Connecticut mineral (*Chathamite*) occurs in mica-slate, associated generally with mispickel and sometimes with copper nickel. Rammelsbergite is found at Schneeberg and at Riechelsdorf.

Cloanthite and smaltin may be regarded as belonging to the same mineral species, indeed the nickel and cobalt are found replacing one another in all proportions without any alteration in the crystalline form of the mineral (see Dana, ii. 57). There are also minerals, still occurring in the same forms, in which the number of atoms of arsenic is to that of the positive metals (nickel, cobalt, iron) as 4 : 3 and as 3 : 2, the percentage of arsenic in the former being about 75, and in the latter 78 or 79. These monometric arsenides of nickel and cobalt may therefore be included in the general formula $R^mAs^n$, where R stands for nickel, cobalt, and iron (regarded as monatomic metals) replacing one another isomorphously. (*Rammelsberg's Mineralchemie*, p. 25.)

**NICKEL, ARSENIOSULPHIDE OF.** See NICKEL-GLANCE (p. 43).

**NICKEL, BROMIDE OF.** $NiBr$ or $Nni''Br^2$.—The anhydrous bromide obtained by passing bromine-vapour over red-hot nickel-filings, forms shining yellow scales soluble in water, alcohol and ether; the aqueous solution yields by evaporation green crystals of the hydrated bromide $Nni''Br^2.3H^2O$.

Bromide of nickel unites with ammonia, either in the dry or in the wet way, forming the compound $NiBr.3NH^3$ or $Nni''Br^2.6NH^3$. It forms light blue crystals, soluble in a small quantity of water, but decomposed on diluting the solution.

**NICKEL, CARBONATE OF.** Occurs native as *Emerald-nickel* (see CARBONATES, i. 789).

**NICKEL, CHLORIDE OF.** $NiCl$ or $Nni''Cl^2$.—Obtained by heating nickel-filings to low redness in a stream of chlorine, or by gently heating the hydrated chloride. It is volatile and sublimes at an incipient red heat, in golden-yellow scales like mosaic gold. It is decomposed by hydrogen at a red heat, yielding a shining coherent mass of metallic nickel.

Anhydrous chloride of nickel dissolves in water after prolonged boiling, yielding a solution of a fine green colour, which may be likewise formed by dissolving the oxide or carbonate of nickel in hydrochloric acid. This solution, when evaporated, deposits the hydrated chloride, $Nni''Cl^2.9H^2O$, in green crystals, which when exposed to the air, deliquesce or effloresce slightly, according to the quantity of moisture present. Chloride of nickel dissolves slightly also in *alcohol*.

Anhydrous chloride of nickel absorbs ammonia gas, forming the *ammonio-chloride*, $NiCl.3NH^3$, analogous to the ammonio-bromide above described (H. Rose). The same compound is obtained in blue octahedrons by dissolving chloride of nickel in warm caustic ammonia in a closed vessel. (Erdmann.)

*Chloride of Nickel and Ammonium*, $NH^4Cl.Nni''Cl^2.6H^2O$, is deposited on mixing 1 pt. of hydrochloric acid saturated with ammonia, and 2 pts. of the same acid saturated with carbonate of nickel, in deliquescent crystals isomorphous with the corresponding magnesium-salt. (Hantz.)

**NICKEL, DETECTION AND ESTIMATION OF.** 1. *Blowpipe Reactions.*—All nickel-salts heated with *carbonate of sodium* on *charcoal* in the inner flame are easily reduced to a grey metallic powder, which is attracted by the magnet. With *borax* they give, in the outer flame, a clear bead which is hyacinth-red while hot, and pale or dark yellow (according to the quantity of nickel present) on cooling; the addition of nitrate or any other salt of potassium gives a blue or dark purple colour to the bead. In the inner flame the bead becomes grey and opaque, owing to the reduction of the metal. With *microcosmic salt* they give in both flames a clear bead which is dark yellow while hot, and almost colourless on cooling. The presence of cobalt, even in small quantity, masks these reactions to a great extent, by the deep blue colour which it produces.

2. *Reactions in Solution.*—Nickel forms but one class of salts, and these are analogous in composition to the chloride above described; they are green in solution or when they contain water of crystallisation; yellow when anhydrous. Their solutions redden litmus.—*Sulphydric acid* does not precipitate nickel-salts from acid solutions, and only very partially from a neutral solution of a salt of a mineral acid, such as the sulphate or chloride; but acetate of nickel, or any nickel-salt mixed with acetate of sodium, is completely precipitated by sulphydric acid on heating the solution, unless a large excess of acetic acid is present. The precipitated sulphide is black, difficultly soluble in dilute hydrochloric or acetic acid, easily in nitric or nitro-muriatic acid. *Sulphide of ammonium* precipitates sulphide of nickel, slightly soluble in the reagent, forming a dark-brown solution, whence the sulphide is precipitated by boiling. (Hence, a brown colour in the filtrate from the sulphide of ammonium precipitate is a sign of the probable presence of nickel.)—*Hydrocyanic acid* precipitates all the nickel as greenish-white cyanide, from acetate of nickel, or from any nickel-salt mixed with sufficient acetate of sodium.—*Cyanide of potassium* precipitates the cyanide from all nickel-salts; excess of the reagent dissolves the cyanide of nickel, forming a soluble double cyanide of nickel and potassium, which is decomposed by dilute sulphuric or hydrochloric acid, hydrocyanic acid being evolved, and cyanide of nickel precipitated, which requires boiling with excess of acid for its conversion into a soluble nickel-salt. *Ferrocyanide of potassium* gives a greenish-white precipitate; *ferricyanide* a yellowish-green precipitate, both insoluble in hydrochloric acid.—*Phosphate or arsenate of sodium* gives a greenish-white precipitate of phosphate or arsenate of nickel. *Oxalic acid* gradually precipitates all the nickel as greenish-white oxalate, soluble in ammonia; when the solution is exposed to the air, the oxalate of nickel slowly separates out.—*Alkaline carbonates* precipitate an apple-green basic carbonate, soluble with greenish-blue colour in excess of carbonate of ammonium.—*Potash* precipitates the apple-green hydrate, insoluble in excess, soluble in ammoniacal salts.—*Ammonia* does not precipitate nickel-salts when free acid or chloride of ammonium is present; from neutral solutions it partially precipitates the hydrate, which is soluble in excess, forming a blue solution, whence the hydrate is precipitated on the addition of sufficient potash. If but little nickel be present, the ammoniacal solution becomes distinctly blue only after long exposure to the air.—*Alkaline hypochlorites* mixed with *caustic alkali* (a solution of bleaching powder or chloride of soda for example) form a black precipitate of hydrated peroxide of nickel.

3. *Quantitative Estimation.*—Nickel is best precipitated from its solutions by *caustic potash*, which throws down an apple-green precipitate of the hydrated protoxide, and if the liquid be heated, leaves not a trace of nickel in the solution. The precipitate must be washed with hot water, dried, ignited, and weighed; it then consists of pure protoxide of nickel, containing 78·57 per cent. of the metal.

The oxide may also be reduced by heating it to redness in a stream of hydrogen, and the reduced metal weighed after cooling in the stream of gas.

In separating nickel from other metals, it is often necessary to precipitate it by *sulphide of ammonium;* this precipitation is attended with difficulties, because the sulphide of nickel is somewhat soluble in the alkaline sulphide. To make the precipitation as complete as possible, Rose directs that the solution be diluted with a considerable quantity of water, and then treated with sulphide of ammonium, as nearly colourless as it can be obtained, avoiding a large excess of the precipitant and likewise an excess of ammonia; the glass is then to be covered up with filtering paper, and left in a warm place. Under these circumstances, the excess of sulphide of ammonium is decomposed by the oxygen and carbonic acid of the air, without risk of the sulphide of nickel being oxidised. As soon as the supernatant liquid has lost its brown colour, the precipitate is collected on a filter and washed as quickly as possible with water containing a little sulphide of ammonium. It must then be dissolved in nitromuriatic acid, and the nickel precipitated by potash as above.

4. *Separation from other Metals.*—The methods of separating nickel from other metals are for the most part the same as those already described for separating cobalt from the same metals (i. 1045), excepting of course the precipitation with nitrite of potassium, and the other methods which serve for the separation of cobalt from nickel itself. From copper and the other metals of the first group, it is separated by *sulphydric acid;* from the metals of the alkalis and alkaline earths and from magnesium, by precipitation with *sulphide of ammonium*, with the precautions above indicated, and in the case of magnesia, with addition of sal-ammoniac to retain that base in solution.

Nickel may sometimes be separated from the alkali-metals by evaporating the whole to dryness and igniting the mixture in a current of hydrogen, whereby the nickel is reduced to the metallic state and may be separated from the alkaline salts by dissolving out the latter with water. This mode of separation is especially applicable when the metals are in the state of chloride.

From magnesium, nickel may be separated by *cyanide of potassium*. The two metals are first precipitated by an alkaline carbonate, and cyanide of potassium is then added in quantity sufficient to redissolve the magnesium, a fresh quantity of alkaline carbonate is then added, and the whole is evaporated to dryness. On treating the residue with water, the magnesia remains undissolved, while the nickel dissolves as double cyanide, and may be precipitated by sulphide of ammonium as above.

When the magnesium and nickel can be converted into neutral acetates, the separation is easily effected by passing *sulphydric acid gas* through the dilute solution. The nickel is then completely precipitated as sulphide, while the magnesium remains dissolved.

Lastly, the separation of nickel and magnesium may be effected by treating the solution with a mixture of *hypochlorite* and *hydrate of potassium* or *sodium*, whereby peroxide of nickel is precipitated, mixed or combined with hydrate of magnesium; and the precipitate after thorough washing, is digested with an excess of solution of *mercuric chloride*. A double chloride of magnesium and mercury is thereby formed, and the magnesia remains dissolved, an equivalent quantity of oxychloride of mercury being at the same time precipitated. The solution is evaporated to dryness, the residue calcined and treated with pure nitric acid, the resulting solution evaporated to dryness, and the residue of nitrate of magnesium calcined and weighed as magnesia. The peroxide of nickel is also ignited to drive off the mercury with which it is mixed, and finally reduced to the metallic state by ignition in a current of hydrogen. (H. Rose, *Traité de Chimie Analytique*, 1861, ii. 213.)

From barium, strontium, and calcium, nickel may be separated by *cyanide of potassium* in the same manner as from magnesium.

From aluminium nickel may be separated by the same processes as cobalt (i. 1045), also by *cyanide of potassium* in the manner just described for magnesium; or by *carbonate of barium*, which precipitates the aluminium and not the nickel.

From iron (in the ferric state) nickel may be separated by *succinate of ammonium* or by *acetate of sodium*, or by digesting the precipitated sulphides in *dilute hydrochloric acid* as described for cobalt (i. 1046); from manganese by the last mentioned method; also by *pentasulphide of calcium*, or by *cyanide of potassium*, or by igniting the mixed chlorides in an atmosphere of *hydrogen*, exactly as described for cobalt; from zinc also by this last method, or by converting the two metals into acetates, adding a large excess of acid, and precipitating the zinc with *sulphydric acid* as for cobalt. From uranium, nickel is separated by precipitating the former metal in the state of uranic oxide with *carbonate of barium*.

The methods of separating nickel from cobalt have been already described (i. 1046). Liebig's method may be advantageously modified as follows:—Instead of treating the solution of the mixed cyanides with mercuric oxide, a solution of *hypochlorite of sodium* is added in excess to the boiling alkaline liquid, in quantity sufficient to destroy the free cyanide of potassium. The nickel is thereby precipitated as peroxide in the form of an intensely black powder, which is easy to wash, and may then be converted by ignition into the protoxide, in which state it may be weighed. Traces of nickel which escape discovery by other methods may thus often be detected in cobalt. Care must be taken to ascertain the absence of manganese, as it would go down with the nickel, accompanied also by traces of iron if the latter metal were present. (*Miller's Elements of Chemistry*, 3rd ed. pt. ii. p. 568.)

*Analysis of Nickel-ores.*—Most of these ores contain large quantities of arsenic, the separation of which by precipitation with sulphydric acid is a long and tedious process. A better method is to fuse the finely divided compound with six times its weight of a mixture of equal portions of nitre and carbonate of sodium, extract the alkaline arsenate thus formed with water, and dissolve the remaining oxides in hydrochloric acid. Or the compound may be fused with three times its weight of sulphur and carbonate of potassium, the alkaline sulpharsenate extracted with water, and the residual sulphides dissolved in hydrochloric acid with gradual addition of nitric acid. The acid solution, in either case, is then nearly neutralised with carbonate of sodium, acetate of sodium is added, and the whole is heated to boiling, whereby all the iron is precipitated. The filtrate is acidulated with hydrochloric acid and saturated with sulphydric acid (to remove copper, bismuth, &c.) and filtered; the filtrate is heated to expel sulphydric acid; and the cobalt and nickel are precipitated by carbonate of sodium, and separated by one of the methods above referred to. Or the ore is dissolved in strong hydrochloric acid, with gradual addition of nitric acid; the solution is heated to boiling and nearly neutralised with carbonate of sodium, with addition of acetate of sodium, and (unless the precipitate has a reddish-brown colour) of ferric chloride also; the liquid, after boiling for some time, is filtered from the basic ferric arsenate thus produced; and the filtrate, which is now free from arsenic and iron, is treated as before. (*Conington's Manual of Chemical Analysis*, p. 143.)

5. *Atomic Weight of Nickel.*—Rothoff (Pogg. Ann. viii. 184), by converting a weighed quantity of nickel-oxide into chloride, and determining the amount of chlorine contained therein by precipitation with nitrate of silver, found the atomic weight of nickel to be $Ni = 29{\cdot}5$, or $Nni = 59$. Erdmann and Marchand (Ann. Ch. Pharm. lxxxii. 76), by the analysis of the protoxide, found $Ni = 29{\cdot}27—29{\cdot}38$. Schneïder (Ann. Ch. Pharm. civ. 220), from the analysis of oxalate of nickel, found, as a mean of four experiments, $Ni = 29$. Dumas (Ann. Ch. Pharm. cxiii. 24), by the same method as Rothoff, found $Ni = 29{\cdot}5$; and lastly, W. J. Russell (Chem. Soc. J. xvi. 58), by reducing pure protoxide of nickel in an atmosphere of hydrogen, finds, as a mean of several experiments, $Ni = 29{\cdot}37$ or $Nni = 58{\cdot}74$.

**NICKEL, EMERALD.** Native hydrocarbonate of nickel, $Nni''CO^3.2Nni''H^4O^4$. (See CARBONATES, i. 789.)

**NICKEL, FLUORIDE OF.** NiF or $Nni''F^2$.—Obtained by dissolving oxide of nickel in hydrofluoric acid, and separates from the acid solution in irregular green crystals. It unites with the fluorides of the alkali-metals, forming very soluble double fluorides which are deposited in granular crystals on evaporation. *Fluoride of nickel and aluminium* separates by evaporation from a mixed solution of the component fluorides, in green needles which dissolve in water slowly, but completely.

*Silicofluoride of nickel* crystallises in green hexagonal prisms.

**NICKEL, IODIDES OF.** NiI or $Nni''I^2$.—When pulverulent nickel is heated in iodine-vapour, a mixture of iodide of nickel with metallic nickel and the oxide is formed, from which the pure iodide may be obtained by substitution, also by heating the hydrated iodide. It forms iron-black metallic shining scales which become moist on contact with the air, form a red-brown solution with a small quantity of water, and a green solution with a larger quantity. This solution may also be prepared by dissolving hydrate of nickel in hydriodic acid, or by treating finely divided nickel with water and excess of iodine. When evaporated, it deposits the hydrated iodide, $Nni''I^2.6H^2O$, in deliquescent crystals, which when heated in contact with the air, give off a little iodine, yield a sublimate of the anhydrous iodide, and leave a residue of nickel-oxide. The aqueous solution dissolves a considerable quantity of iodine, which colours it brown-red.

An *oxyiodide of nickel* is formed by digesting the solution of the iodide with hydrate of nickel, or by evaporating the same solution quickly to dryness in contact with the air, and dissolving out the undecomposed iodide from the residue with water.

Anhydrous iodide of nickel absorbs *ammonia gas* when heated in it, forming the yellowish-white compound $NiI.2NH^3$ or $Nni''I^2.4NH^3$. By dissolving the iodide in hot aqueous ammonia, blue octahedrons are obtained consisting of $NiI.3NH^3$ or $Nni''I^2.6NH^3$, sparingly soluble in water and in aqueous ammonia. The ammoniacal solution mixed with alcohol yields a green precipitate containing ammonia.

**NICKEL, NITRIDE OF.** Formed, according to Schrötter, by heating protoxide of nickel to 206° in ammonia-gas.

**NICKEL, OXIDES OF.** Nickel forms two oxides, a protoxide and a sesquioxide; the former only is a salifiable base.

*Protoxide*, $Ni^2O$ or $Nni''O$.—This oxide is obtained in the anhydrous state by calcining the nitrate, hydrate or carbonate of nickel, or by heating metallic nickel with nitre. It may be freed from traces of peroxide which it sometimes contains, by heating it to about 100° in hydrogen-gas (Erdmann). Russell (Chem. Soc. J. xvi. 58) prepares it by calcining oxalate of nickel, dissolving the residue in nitric acid, evaporating, and exposing the residue to strong and continued ignition over a gas furnace. It is a dense green or greyish-green, non-magnetic powder, which does not absorb oxygen from the air, either at common or at higher temperatures. It is reduced to the metallic state by hydrogen at a red heat, and by charcoal at a white heat.

Anhydrous oxide of nickel has been found crystallised on the surface of black copper (ii. 30) reduced from nickeliferous copper ores, in microscopic regular octahedrons, opaque with metallic lustre, non-magnetic, and having a specific gravity of 6·605, insoluble in nitric, hydrochloric, and even nitro-hydrochloric acid, and dissolving with difficulty in boiling sulphuric acid (Genth). Similar crystals of anhydrous nickel-oxide have been found by Bergemann (J. pr. Chem. lxxv. 253), together with native

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bismuth, in cavities of a mineral chiefly consisting of arsenate of nickel, said to be from Johann-Georgenstadt. Debray (Compt. rend. lii. 985) has obtained protoxide of nickel in the crystalline form by strongly igniting a mixture of sulphate of nickel and sulphate of potassium.

The *hydrated protoxide* or *hydrate of nickel*, NiHO or $\mathrm{Nni''H^2O^2}$, is obtained as an apple-green precipitate, by treating the solution of a nickel-salt with excess of caustic potash or soda, and is deposited as a green crystalline powder from a solution of the carbonate in excess of ammonia on standing or evaporation (Pelouze and Frémy). When heated it gives off its water, and leaves the anhydrous protoxide. It dissolves easily in *acids*, forming the nickel salts; also in *ammonia*, forming a violet solution, from which it is precipitated by the fixed alkalis or alkaline earths, the precipitate consisting of a compound of oxide of nickel with the precipitating oxide.

A crystalline hydrate of nickel containing $\mathrm{Nni''H^2O^2.H^2O}$ has been found as an incrustation on chrome-iron at Texas in Pennsylvania. It is transparent, has an emerald-green colour, and a density of 3·05. (Silliman, Sill. Am. J. [2] iii. 40.)

Protoxide of nickel unites with other metallic oxides, playing the part of an acid with strong bases, such as potash (*vid. sup.*) and that of a base with alumina, ferric oxide, &c. When ammonia is added to a solution containing nickel together with metals whose oxides are insoluble in ammonia, the precipitated oxide almost always carries down with it a certain quantity of nickel-oxide: hence this method of separating nickel from other metals does not give exact results in quantitative analysis. The same indeed is true more or less with regard to the separation of all metals by the relative solubilities of their oxides in caustic alkalis, *e.g.* of aluminium and iron by potash.

*Sesquioxide or Peroxide of Nickel*, $\mathrm{Ni^4O^3}$ or $\mathrm{N\overset{'''}{n}i^2O^3}$.—This oxide is produced by calcining the nitrate at a moderate heat. It is a black powder of specific gravity 4·84 (Herapath) which is resolved by ignition into oxygen and the protoxide, and behaves with acids like a peroxide, dissolving in them with evolution of oxygen, and forming solutions of nickel-salts.

A *hydrated sesquioxide*, $\mathrm{N\overset{'''}{n}i^2O^3.3H^2O}$ or $\mathrm{N\overset{'''}{n}iH^3O^3}$, is obtained by treating the hydrated protoxide or the carbonate with chlorine-water or the solution of an alkaline hypochlorite, or by precipitating a nickel-salt with a mixture of caustic alkali and alkaline hypochlorite. It is dark brown while suspended in water, but forms a black shining mass when dry. When heated it readily gives off water and oxygen. With *acids* it behaves like the anhydrous sesquioxide, but dissolves with greater facility. With aqueous *oxalic acid*, it forms oxalate of nickel, with evolution of carbonic anhydride. It dissolves in *ammonia*, with evolution of nitrogen, the solution containing protoxide of nickel.

Another hydrated peroxide of nickel of dingy light-green colour, but unknown composition, is obtained by treating the hydrated protoxide with peroxide of hydrogen. (Thénard.)

**NICKEL, OXYCHLORIDE OF.** Formed by digesting the hydrated protoxide in aqueous chloride of nickel. It is sparingly soluble in water, and turns reddened litmus-paper blue.

**NICKEL, OXYGEN-SALTS OF.** Nickel forms but one class of salts, corresponding in composition to the protoxide, chloride, &c., *e.g.* the nitrate $\mathrm{NiNO^3}$ or $\mathrm{Nni''N^2O^6}$, the sulphate $\mathrm{Ni^2SO^4}$ or $\mathrm{Nni''SO^4}$, the acetate $\mathrm{C^2H^3NiO^2}$ or $\mathrm{C^4H^6Nni''O^4}$, &c. Most of them are soluble in water and are produced by dissolving either of the oxides or the corresponding hydrates in acids, the sesquioxide being first reduced to protoxide; in many cases also, with evolution of hydrogen, by acting on the metal with dilute acids, the pulverulent metal dissolving easily, the compact metal often very slowly. Those nickel-salts which are insoluble in water, and are obtained by precipitation, *e.g.* the carbonate, borate, and phosphate, dissolve readily in nitric, hydrochloric, and sulphuric acid, &c.

Nickel-salts are for the most part emerald or apple-green in the hydrated state, yellow when anhydrous, so that characters traced on paper with a nickel solution turn yellow when heated. Soluble nickel-salts redden litmus slightly, have an astringent metallic taste, and exert an emetic action. Those which contain volatile acids are decomposed by ignition, the inorganic salts generally leaving a residue of protoxide, the organic salts, metallic-nickel. (For their behaviour with reagents, see p. 38.)

**NICKEL, OXYIODIDE OF.** See p. 40.

**NICKEL, PHOSPHIDES OF.** The *tritophosphide*, $\mathrm{Ni^3P}$ or $\mathrm{N\overset{''}{n}i^3P^2}$, is obtained by heating chloride or sulphide of nickel in a current of phosphoretted hydrogen gas. It is black, insoluble in hydrochloric acid, but easily decomposed and dissolved by nitric acid. (H. Rose, Pogg. Ann. xxiv. 322.)

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A phosphide containing only a small quantity of phosphorus is obtained:—1. By passing phosphorus-vapour over red-hot nickel (Davy), or by throwing pieces of phosphorus on it (Pelletier).—2. By fusing nickel with glacial phosphoric acid and charcoal powder (Pelletier), or 6 to 8 pts. nickel-filings or nickel-oxide, with 10 pts. bone-ash, 5 pts. pounded quartz, and 1 pt. charcoal in a charcoal-lined crucible (Berthier). It is silver-white, brittle, much more fusible than nickel, not magnetic.

**NICKEL, SELENIDE OF.** $Ni^2Se$ or $Nni''Se$.—Obtained by igniting metallic nickel in selenium-vapour, as a silver-white, non-magnetic, brittle crystalline mass (apparently monometric), having a dull metallic lustre, and specific gravity = 8·462. It is not attacked by hydrochloric acid, slowly dissolved by nitric acid, completely by nitromuriatic acid. When fused with borax, it yields a golden yellow metallic mass with striated surface. (G. Little, Ann. Ch. Pharm. cxii. 211.)

**NICKEL, SILICATE OF.** See PIMELITE and SILICATES.

**NICKEL, SULPHATE OF.** This salt occurs as a hydrate in capillary interlacing crystals at Wallace mine, Lake Huron, on a sulphide of nickel and iron, mostly as an efflorescence. Kobell's *pyromelin*, occurring as an earthy pale yellow crust, with native bismuth and arsenical nickel, at the Frederich's mine near Bayrent, appears to be the same species. (See SULPHATES.)

**NICKEL, SULPHIDE OF.** Nickel forms with sulphur the three following compounds:

*α. Hemisulphide*, $Ni^4S$ or $\overset{''}{N}ni^2S$. Produced by igniting sulphate of nickel in a current of hydrogen. Pale yellow, metallic-shining, brittle, magnetic mass, which may be melted in glass vessels.

*β. Protosulphide*, $Ni^2$ or $Nni''S$. This compound occurs native as *Capillary Pyrites* (*Haarkies*), in rhombohedral crystals having the length of the principal axis = 0·3295, the angle R : R = 144° 8′, and perfectly cleavable parallel to the rhombohedral faces; more frequently in delicate capillary crystallisations. Hardness = 3—3·5, specific gravity 5·25—5·65 (the mineral from Joachimsthal, 4·001 according to Kenngott). It is brittle, has a brass-yellow colour and metallic lustre, and is bright in the streak. It usually occurs in capillary crystals in the cavities and among the crystals of other minerals, as at Joachimsthal in Bohemia; at Johanngeorgenstadt, Przibram, Riechelsdorf, Andreasberg; in Cornwall, &c.; also in Lancaster County, Pennsylvania.

Protosulphide of nickel is formed, with emission of light, when sulphur is fused in contact with finely divided nickel; it is also produced by the action of sulphur, or a mixture of sulphur and potash on the oxides of nickel at a red heat; and by igniting the protoxide in sulphydric acid gas; lastly, according to Berthier, by reducing sulphate of nickel with charcoal-powder; in this case, however, a small quantity of the hemisulphide is formed at the same time. When prepared by either of these methods it resembles the native sulphide in colour and lustre. It is less fusible than the hemisulphide; is decomposed by ignition in the air, but not in close vessels. It is but slowly decomposed when heated in chlorine gas, and not at all by hydrogen at a red heat. It dissolves slowly in hot nitric or nitromuriatic acid.

*A hydrated protosulphide of nickel* is obtained by the action of sulphydric acid on neutral solutions of nickel-salts containing weak acids, the acetate for example, or by precipitating any neutral nickel-solution with sulphide of ammonium or potassium. It has a dark brown colour, nearly black. It oxidises on exposure to the air, and is converted into soluble sulphate. When heated out of contact with air, it gives off water and melts to a mass of the anhydrous sulphide. When recently precipitated and still moist, it dissolves sparingly in sulphurous acid, also in ammonia and sulphide of ammonium, potassium, &c., forming a brown solution which, on exposure to the air, becomes colourless and deposits sulphide of nickel. The precipitated sulphide is nearly insoluble in acetic or dilute hydrochloric acid, although a very small quantity of free hydrochloric, sulphuric, or even acetic acid, suffices to prevent its formation in solutions of nickel-salts by the action of sulphydric acid. Nitric and nitromuriatic acids dissolve it more readily.

*Disulphide*, $Ni^2S^3$ or $NniS^3$. Obtained by heating a mixture of carbonate of nickel, carbonate of potassium, and sulphur to dull redness. The mass when washed leaves the disulphide in the form of a steel-grey powder, which is decomposed by chlorine, with formation of chloride of nickel and chloride of sulphur.

Sénarmont, by decomposing chloride of nickel with chloride of potassium at 160°, obtained a yellowish sulphide of nickel having the composition $Nni^3S^4$ or $NniS.Nni^2S^3$.

**NICKEL AND IRON, SULPHIDE OF.** $(\frac{1}{3}Nni.\frac{2}{3}Ffe)''S$.—Occurs near Lillehammer in southern Norway, in monometric crystals with octahedral cleavage, or in granular masses. Hardness = 3·5—4. Specific gravity = 4·6. It is not magnetic, has a bronze-yellow colour, and light bronze-brown streak. Contains 22·28 per cent. nickel, 40·86 iron and 36·86 sulphur. It occurs with copper pyrites in hornblende rocks, and is worked for the extraction of nickel. An impure variety, slightly mixed with magnetic iron ore, is found at Inverary in Argyleshire.

**NICKEL-BLOOM.** See NICKEL, ARSENATE OF (p. 35).

**NICKEL-BOURNONITE.** Bournonite or sulphantimonite of lead and copper (i. 651) from Wolfsberg, in which lead is partly replaced by nickel and cobalt, contains 19·87 per cent. sulphur, 24·28 antimony, 3·22 arsenic, 35·52 lead, 9·05 copper, 5·47 nickel and cobalt, and 0·84 iron (= 98·25). (Rammelsberg, Pogg. Ann. lxxvii. 253.)

**NICKEL-GLANCE.** A mineral species analogous to cobalt-glance (i. 1057) in form and composition, and expressible chemically by the formula $Ni''S(As ; Sb)$ or $NniS(As ; Sb)$ or $NniS^2.Nni(As ; Sb)^2$, the arsenic and antimony being sometimes present together, sometimes singly, thus forming the three varieties, *antimonial*, *arsenical* and *antimonio-arsenical nickel-glance.*

The crystals of this species belong to the monometric system, being for arsenical nickel-glance, cubes, octahedrons, and the intermediate forms shown in figures 174, 175, 176 (CRYSTALLOGRAPHY), and combinations of the pentagonal dodecahedron with the cube (fig. 211) and octahedron. For the varieties containing antimony the prevailing form is the octahedron modified by faces of the cube. Cleavage cubic in all varieties. The mineral likewise occurs massive, with granular structure; the purely arsenical variety also lamellar. Hardness = 5—5·5. Sp. gr. = 5·6—6·9 (of the antimonial varieties, 6·2—6·5). Lustre metallic. Colour silver-white to steel-grey. Streak greyish-black. Fracture uneven. Brittle.

*Analyses:* 1. *Antimonial.—a.* From the Landskrone mine in Siegen, Westphalia; mean of two analyses (H. Rose, Pogg. Ann. xv. 588).—2. *Antimonio-arsenical.—b.* Albertine mine near Harzgerode in the Hartz (Rammelsberg, *ibid.* lxviii. 511).—*c.* Sayn-Altenkirchen (Ullmann, *Rammelsberg's Mineralchemie*, p. 63).—*d.* Freusburg (Klaproth, *Beiträge*, vi. 329).—3. *Arsenical. e.* Haueisen near Lobenstein in Thuringia: sp. gr. 5·954 (Rammelsberg, *loc. cit.*).—*f.* Jungfer mine near Müsen: crystallised (Schnabel, *Ramm. Mineralch.* p. 62).—*g.* Pfingstwiese near Ems: crystallised, with faces of the pentagonal dodecahedron (Bergemann, J. pr. Chem. lxxv. 244).—*h.* Albertine mine near Harzgerode (Rammelsberg, *loc. cit.*).—*i.* Mercury mine near Ems: massive (Schnabel, *loc. cit.*).

| | Antimonial. | Antimonio-arsenical. | | | Arsenical. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
| Sulphur . | 15·77 | 17·38 | 16·40 | 15·25 | 20·16 | 18·94 | 19·04 | 18·83 | 17·82 |
| Antimony . | 54·61 | 50·84 | 47·56 | 47·75 | . . | . . | 0·61 | 0·86 | |
| Arsenic . | . . | 2·65 | 9·94 | 11·75 | 48·02 | 46·02 | 45·02 | 44·01 | 38·92 |
| Nickel . | 27·70 | 29·43 | 26·10 | 25·25 | 31·82 | 32·66 | 34·18 | 30·30 | 35·27 |
| Cobalt . | . . | . . | . . | . . | . . | . . | 0·27 | . . | 2·23 |
| Iron . | . . | 1·83 | . : | . . | . . | 2·38 | 1·02 | 6·00 | 4·97 |
| Copper . | . . | . . | . . | . | . . | . . | . . | . . | 2·75 |
| | 98·08 | 102·13 | 10·00 | 10·00 | 10·00 | 10·00 | 100·14 | 10·00 | 101·96 |

There are also varieties of nickel-glance differing somewhat in composition from the above, so far at least as the analyses can be trusted, viz. 1. *Amoibite*, occurring in small steel-grey octahedrons (hardness = 4) at Lichtenberg in the Fichtelgebirge (v. Kobell, J. pr. Chem. xxxiii. 403);—2. *Gersdorffite* from Schladming in Styria, where it occurs both crystallised (Pless. Ann. Ch. Pharm. li. 250) and massive (Löwe, Pogg. Ann. lv. 503);—3. Nickel-glance from Prakendorf in Hungary (Löwe).

| | Amoibite. | Gersdorffite. | | | Nickel-glance from Prakendorf. |
|---|---|---|---|---|---|
| | | *crystallised.* | | *massive.* | |
| Sulphur . . . | 13·87 | 16·11 | 16·35 | 14·22 | 16·25 |
| Arsenic . . . | 45·34 | 39·88 | 39·04 | 42·52 | 46·10 |
| Nickel . . . | 37·34 | 27·90 | 19·59 | 38·42 | 28·75 |
| Cobalt . . . | trace | 0·83 | 14·12 | | |
| Iron . . . | 2·50 | 14·97 | 11·13 | 2·09 | 8·90 |
| Silica . . . | . . | . . | . . | 1·87 | |
| | 99·05 | 99·69 | 100·23 | 99·12 | 100·00 |

Rammelsberg suggests that sulphide of nickel, $Nni''S$, may be monometric, like many sulphides of the form $M''S$, and in that case, since the arsenide, $NniAs^2$, is likewise monometric, these nickel-glances may be regarded as isomorphous mixtures having the composition $m\mathrm{Nni''S}.n\mathrm{NiAs^2}$ or $\mathrm{Nni(S; As^2)}$.

**NICKEL-LINNÆITE.** *Siegenite.* Linnæite (cobaltoso-cobaltic sulphide, i. 1050) in which a considerable proportion of the cobalt is replaced by nickel. *a.* From Siegen in Prussia, where it occurs in octahedrons (Schnabel, *Rammelsberg's Mineralchemie*, p. 110).—*b.* From the same locality (Ebbinghaus, *loc. cit.*).—*c.* Finksburg Carroll County, Maryland: pale steel-grey, with a yellowish tinge; distinct cubic cleavage; intergrown with copper pyrites (Genth, Sill. Am. J. [2] xxxiii. 415).—*d.* La Matte, Missouri: seldom crystalline, sometimes however exhibiting the forms O and O . ∞O∞; cleavage very indistinct; colour, between steel-grey and tin-white (Genth, *loc. cit.*):

| | S. | Ni. | Co. | Fe. | Cu. | Pb. | Gangue. | | |
|---|---|---|---|---|---|---|---|---|---|
| *a.* | 41·98 | 33·64 | 22·09 | 2·29 | . . | . . | . . | = | 100 |
| *b.* | 42·30 | 42·64 | 11·0 | 4·69 | . . | . . | . . | = | 100·63 |
| *c.* | 39·70 | 29·56 | 25·69 | 1·96 | 2·23 | . . | 0·45 | = | 99·59 |
| *d.* | 41·54 | 30·53 | 21·34 | 3·37 | . . | 0·39 | 1·07 | = | 98·24 |

**NICKEL-PYRITES.** *Capillary Pyrites.* Native sulphide of nickel (p. 42).

**NICKEL-VITRIOL.** Sulphate of nickel (see p. 42, also SULPHATES).

**NICOTIANINE.** *Tobacco-camphor.* $\mathrm{C^{23}H^{32}N^2O^3}$.—A white crystalline substance obtained by distilling tobacco-leaves with water. It is soluble in water, alcohol, and ether; melts when heated and then gradually evaporates. (Hermbstädt, Schw. J. xxxi. 442; Barral, Compt. rend. xxi. 1376.)

**NICOTIC ACID.** $\mathrm{C^8H^4O^4}$. A crystallisable dibasic acid found in tobacco-juice by Barral (Compt. rend. xxi. 1374). According to other chemists, however, the only acids contained in tobacco-juice are malic and citric acids.

**NICOTINE.** $\mathrm{C^{10}H^{14}N^2}$. (Gm. xiv. 219; Gerh. iv. 184.)—Vauquelin in 1809 ascertained that the acrid principle of tobacco was volatile, and capable of separation from its compounds by means of a fixed alkali. Posselt and Reimann in 1828 succeeded in obtaining it in a state of comparative purity from the leaves of *Nicotiana Tabacum*, *Macrophylla rustica* and *M. glutinosa*. For a long time nicotine was supposed to have the formula $C^{10}H^8N = \mathrm{C^5H^8N}$, which was subsequently altered to $C^{10}H^7N = \mathrm{C^5H^7N}$, in accordance with the more accurate analyses of Melsens and Schlœsing; but Barral, by a determination of its vapour-density, showed it to possess in the free state a condensation twice as great as this, its formula becoming therefore $C^{20}H^{14}N^2$ = 4 volumes of vapour, or in accordance with modern ideas $\mathrm{C^{10}H^{14}N^2}$ = 2 volumes. It is considered however by some chemists that in forming certain compounds, nicotine breaks up, as it were, into two groups, having the composition $\mathrm{C^5H^7N}$, each equal to $\mathrm{H^3}$. The experiments of Kekulé and v. Planta, who treated nicotine with the iodides of the alcohol-radicles, indicate unmistakably the fact that in nicotine the group $\mathrm{C^5H^7}$ is equivalent to $\mathrm{H^3}$. The molecule of nicotine is therefore derived from two molecule of ammonia in which the hydrogen is replaced by $\mathrm{C^5H^7}$, thus:—

$$\mathrm{C^{10}H^{14}N^2} = \left\{\begin{matrix}\mathrm{N(C^5H^7)} \\ \mathrm{N(C^5H^7)}\end{matrix}\right. \text{derived from } \left\{\begin{matrix}\mathrm{NH^3} \\ \mathrm{NH^3}\end{matrix}\right.$$

This explains why, in treating nicotine with oxalic acid and with chloride of benzoyl, no substances are obtained analogous to oxanilide or benzanilide (Gerh. iv. 185). On the other hand, most chemists of the present day will prefer to regard nicotine as a diamine. There is indeed no sufficient evidence to show that any splitting up of nicotine takes place under the influence of the iodides of the alcohol-radicles. We shall therefore assume in this article that the compounds assumed by Gerhardt to contain one atom of methyl, ethyl, &c., contain twice that number, and that the vapour-density correctly represents the molecule of nicotine which enters into *all* its known combinations.

*Preparation.*—1. Tobacco-juice is treated with excess of solution of hydrate of potassium; the mixture is then shaken up with benzene or ether in stoppered bottles; the ether is decanted and distilled at a gentle heat sufficient to volatilise the ether; and the heat is afterwards raised to a sufficient temperature to drive over the nicotine. —2. A mixture of lime and powdered tobacco is placed in a cylinder and a current of steam from a boiler is sent in, the other end of the cylinder being connected with a condensing worm. The liquid which comes over contains nicotine, ammonia, and some other bases not yet examined. The liquid is neutralised with sulphuric acid and the solution concentrated by evaporation. When sufficiently concentrated it is treated with ammonia to liberate the nicotine, and ether is then added: the ethereal solution on evaporation yields the nicotine almost pure. It may be further purified by rectification (Debize, Compt. rend. l. 874).—3. Tobacco in very small pieces is digested with dilute sulphuric acid for three days and then pressed. The residue is repeatedly treated in this manner until it has lost its acrid taste; and the liquid so obtained is evaporated to half and then distilled with lime. The distillate, which contains the nicotine, must be shaken up with ether, and the latter, after decantation, distilled. The ether readily distils away, leaving the nicotine in an impure state. It is to be kept warm for a considerable time and then heated to 140°, at which temperature it will give off ammonia and other less volatile impurities. Lime is to be added to the residue, and the mixture distilled in an oil-bath at 190°, in a current of hydrogen. The product of this operation redistilled in a current of hydrogen yields the nicotine pure and colourless (Barral).—4. Tobacco is treated with water, and the solution concentrated; the extract is dissolved in alcohol, which after decantation is likewise concentrated; and this last extract is treated with hydrate of potassium, then agitated with ether, to dissolve the nicotine and also some foreign substances, which are got rid of by precipitating the alkaloïd in the state of oxalate. This precipitate is washed by agitating it with ether, then treated with potash, again dissolved in ether, and submitted to distillation. The residue of the distillation is coloured but limpid, and contains, besides nicotine, water, ether, and ammonia; a temperature of 140°, maintained for 12 hours, and assisted by a current of dry hydrogen, suffices to expel these three bodies, so that the nicotine passes over pure and colourless, when the temperature is subsequently raised to 180°.—Two lbs. of good tobacco, grown in the department of Lot, are capable of yielding by this process from 50 to 60 grammes of nicotine. (Schlœsing.)

The amount of nicotine in leaf or manufactured tobacco may be accurately ascertained by a simple and easy process. Ten grammes of tobacco are exhausted with ammoniacal ether in a continuous distillatory apparatus, the ammoniacal gas is expelled from the nicotine solution by boiling; the liquid is then decanted, and, after evaporation of the ether, neutralised by a solution of sulphuric acid of known strength. (Schlœsing, Compt. rend. Dec. 1846, Chem. Gaz. 1847, 43.)

*Extraction of nicotine from the contents of the stomach, or from the substance of animal tissues in cases of poisoning.*—1. For this purpose it is only necessary to add excess of hydrate of potassium and repeatedly extract with ether or pure benzene. On evaporation in a retort at a gentle heat, the nicotine will remain in an impure state. It may then be converted into a sulphate, the solution filtered, and the nicotine re-obtained by a repetition of the first process by means of hydrate of potassium and ether. —2. Or the contents of the stomach may be repeatedly exhausted by a dilute acid, and the filtered and evaporated solution may be made to give up its nicotine in the manner previously indicated. (See also ALKALOÏDS, DETECTION OF, IN CHEMICO-LEGAL INVESTIGATIONS, vol. i. p. 125.)

The following table contains the percentage of nicotine in various kinds of tobacco according to the experiments of Schlœsing:—

| Names of the tobacco. | Nicotine in 100 parts of the dried tobacco. | Names of the tobacco. | Nicotine in 100 pts. of the dried tobacco. |
|---|---|---|---|
| Lot . . . . | 7·96 | Alsace . . . | 3·21 |
| Lot-et-Garonne . . | 7·34 | Virginia . . . | 6·87 |
| Nord . . . | 6·58 | Kentucky . . | 6·09 |
| Ille-et-Vilaine . . | 6·29 | Maryland . . | 2·29 |
| Pas-de-Calais . . | 4·94 | Havannah . . | 2·00 |

*Properties.*—Colourless transparent oil, which does not freeze at −10°, it gives off excessively irritating vapours when heated, and boils at 250° (Barral). Its specific gravity at various temperatures is as follows:

| Temp. . . | 4° | 15° | 30° | 50° | 101·5° |
|---|---|---|---|---|---|
| Sp. gr. . . | 1·033 | 1·027 | 1·018 | 1·0006 | 0·9424 |

Nicotine has a burning taste even when very much diluted, and causes choking. When it is placed on the tongue of a dog in a fatal dose, the epithelium separates after death with facility (Orfila). It dilates the pupil when taken internally (Orfila). 5 milligrammes sufficed to kill a middle-sized dog in 3 minutes. When $\frac{1}{8}$th of a grain was dropped into the eye of a cat, *contraction* of the pupil took place followed by narcotic symptoms which passed off in an hour. Nicotine has a strong alkaline reaction; it strongly deflects the plane of polarisation to the left. At 100° it dissolves 10·58 per cent. of *sulphur*. It is very soluble in *water*, *alcohol*, *ether*, and *fat oils*. Dissolves in any quantity in *turpentine* and hydrocarbons having similar solvent powers. Vapour-density (after allowing for a residue of 3 per cent. in the balloon) 5·607; calc. 5·616.

*Decompositions.*—1. Nicotine rectified ever so carefully in a current of hydrogen becomes rapidly yellow and finally brown when exposed to light or air.—2. It always leaves a resinous residue when distilled.—3. Burns with a bright smoky flame in a lamp with a wick.—4. Evolves inflammable vapours when heated to its boiling point.—5. Boiling *sulphuric acid* decomposes it entirely.—6. Heated with *tincture of iodine* it yields tri-iodonicotine (Wertheim).—7. When it is dropped into *chlorine*, violent action takes place sometimes accompanied with emission of light; and a red colour is developed, which however disappears on exposure to light for some days. This decolorised fluid treated with water, yields a white substance which crystallises from alcohol.—8. Hydrochlorate of nicotine treated with *chlorine* yields a crystallised substance soluble in water but insoluble in alcohol.—9. Nitric acid decomposes it, yielding a liquid from which alkalis disengage a volatile base, probably ethylamine (Anderson).—10. When the alcoholic solution is treated with gaseous *cyanogen*, a brown non-basic substance is formed (Hofmann, Stahlschmidt).—11. *Cyanate of ethyl* forms with nicotine a compound crystallising in beautiful laminæ. (Wurtz.)

*Reactions of Nicotine.*—1. Nicotine in aqueous solution gives with *tincture of iodine* a yellowish turbidity becoming crimson, this reaction occurring even when the nicotine solution contains only $\frac{1}{1000}$ of base (Posselt and Reimann). According to v. Planta, the precipitate is of a kermes-brown colour. (Probably the tint changes as the quantity of iodine tincture becomes larger.)—2. Aqueous solution of nicotine gives white precipitates with solution of *acetate of lead, mercuric chloride, stannous and stannic chlorides, salts of zinc, and gallotannic acid;* with *platinic chloride*, a yellow precipitate; with *ferric salts*, an ochre-yellow precipitate not soluble in excess of base; with *trichloride of gold*, a reddish-yellow precipitate. With *chloride of cobalt*, a blue precipitate is formed becoming green and slightly soluble in excess of base. When *perchloride of antimony* is added drop by drop to a solution of phosphoric acid, a liquid is obtained which gives a slight turbidity in an aqueous solution of nicotine containing $\frac{1}{250}$th (Schulze). With *phosphate of magnesium*, an aqueous solution of nicotine gives a gelatinous precipitate. *Hydrochloric* solution of nicotine gives with solution of *platinic chloride* a yellow crystalline precipitate if the solutions are strong; but if weak, four-sided prisms are deposited after a time. A similar solution of nicotine gives with *picric acid*, sulphur yellow flocks, with *auric chloride*, light yellow flocks, sparingly soluble in hydrochloric acid.—3. *Nitric acid* partially decomposes nicotine, with evolution of red fumes, the solution when boiled becoming of a reddish-brown colour similar to the tint of a strong solution of platinic chloride. *Phospho-molybdic acid* gives with nicotine and its salts a bright bulky yellow precipitate. (Sonnenschein).

**Salts of Nicotine.** *Sulphate of Nicotine* is uncrystallisable, very soluble in water and in alcohol. 100 pts. of sulphuric acid neutralise 329·7 of nicotine, corresponding to the formula $2C^{10}H^{14}N^2H^2.SO^4$.—The *nitrate* crystallises with difficulty.—The *hydrochlorate*, $C^{10}H^{14}N^2.2HCl$, is a deliquescent salt which may be obtained in long fibrous crystals by treating nicotine with gaseous hydrochloric acid, and keeping the product for a time in vacuo. The alcoholic solution deflects the plane of polarisation to the right.—The *phosphate* is obtained by neutralising an aqueous solution of phosphoric acid with nicotine, as a syrupy liquid which yields large laminar crystals resembling cholesterin.

*Oxalate of Nicotine* forms crystals very soluble in water and boiling alcohol, insoluble in ether.—The *acetate* is a syrupy liquid soluble in ether.—The *tartrate* forms granular crystals very soluble in water.

*Double salts of Nicotine.* *Platinum-salt*, $C^{10}H^{14}N^2.2HCl.2PtCl^2$.—When a solution of platinic chloride is added to a strong hydrochloric solution of nicotine, a yellow crystalline precipitate is obtained. If the solutions are dilute, four-sided prisms will gradually form, or sometimes large ruby-red crystals. The salt is very soluble in slight excess of nicotine; dissolves with difficulty in cold, but more easily in boiling water, is insoluble in alcohol and in ether.

*Compounds of Nicotine with Protochloride of Platinum.* *a.* $C^{10}H^{14}N^2.4HCl.2PtCl$. When nicotine is gradually added to a hydrochloric solution of platinous chloride, the mixture being agitated, an orange-yellow precipitate is obtained having the above composition (Raewsky). It is insoluble in cold water, but soluble in boiling water, and is deposited from the latter solution on standing in the crystalline form.

*β.* When the mother-liquor of the above salt is evaporated, red prisms are obtained containing only 2 atoms of hydrochloric acid, $C^{20}N^2H^{14}.2PtCl.2HCl$. (Raewsky.)

*Gold-salt.* Hydrochlorate of nicotine added to a solution of auric chloride throws down a pale yellow flocculent precipitate, almost insoluble in hydrochloric acid. (v. Planta.)

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*Mercury-salt, of Nicotine.* 1. With *Mercuric Chloride.* α. $C^{10}H^{14}N^2.Hg''Cl^2$.—Obtained by precipitating a solution of mercuric chloride by a solution of nicotine.—White crystalline precipitate, insoluble in water and in ether, almost insoluble in alcohol. Melts below 100°. (Ortigosa.)

β. $C^{10}H^{14}N^2.3Hg''Cl^2$.—Obtained by adding a saturated solution of mercuric chloride to a dilute solution of nicotine in hydrochloric acid, until a permanent precipitate begins to be formed. The turbid liquid when left at rest for some days, yields the salt in colourless or yellowish crystals often an inch long, sparingly soluble in alcohol or cold water, dissolving readily and without decomposition in water acidulated with hydrochloric acid, decomposed by boiling with water. (Bödeker.)

γ. $C^{10}H^{14}N^2.HCl.4Hg''Cl^2$. Crystalline precipitate obtained by adding a cold neutral solution of hydrochlorate of nicotine to a large excess of aqueous solution of mercuric chloride. Dissolves in boiling water, yielding on cooling radiating groups of needles.

*Cyano-chloromercurate of Nicotine.* Obtained on adding to a dilute solution of neutral hydrochlorate of nicotine, about an equal volume of a saturated solution of mercuric cyanide. It is deposited in tufts of silky needles. Dissolves easily in cold or boiling water, and in alcohol. The solution is not precipitated by hydrate of potassium even on heating. Treated with hydrochloric acid, it evolves hydrocyanic acid. Its formula has not been determined with certainty.

2. With *Mercuric Iodide.* α. $C^{10}H^{14}N^2.Hg''I^2$.—Colourless crystals obtained by triturating nicotine with mercuric iodide, and subsequently treating the mass with boiling water. The reaction is so energetic that sufficient heat is evolved to vaporise part of the nicotine.

β. $C^{10}H^{14}N^2.Hg''I^2.2HI$. To prepare this salt, nicotine is dissolved in dilute hydriodic acid, and a solution of mercuric iodide in hydriodic acid is added until the precipitate ceases to be redissolved, and the solution becomes turbid. The salt soon begins to crystallise. The mother-liquor cannot be concentrated without decomposition. Yellow prisms sparingly soluble in cold water and in alcohol. Decomposed by boiling water, with separation of a reddish-yellow resinous matter. Insoluble in solution of hydrate of potassium.

*Nicotine with Nitrate of Silver.* α. $C^{10}H^{14}N^2.NO^3Ag$.—Colourless prisms obtained on mixing a cold dilute alcoholic solution of nicotine with an excess of an alcoholic solution of silver nitrate.

β. $2C^{10}H^{14}N^2.NO^3Ag$. Prepared like the preceding, but employing an excess of nicotine. It is deposited in a dilute solution and by spontaneous evaporation in fine prisms.

*Compound of Nicotine with Iodine,* $(C^{10}H^{14}N^2)^2I^2$.—Ethereal solutions of iodine and nicotine combine when mixed, evolving sufficient heat to make the ether boil. In a short time the mixture becomes filled with crystals. In more dilute solutions the substance is deposited in the form of ruby-red needles (Wertheim). The compound melts at 100° without decomposition. It is decomposed in the cold by solution of hydrate of potassium, nicotine being liberated and iodide and iodate of potassium being formed.—A *hydrochlorate,* $(C^{10}H^{14}N^2)^2I^2.2HCl$, is obtained in fine, clear, ruby-red crystals, by cautiously saturating with hydrochloric acid a very weak alcoholic solution of the iodine-compound, and placing the liquid in vacuo.

### *Methyl-, Ethyl-, and Amyl-derivatives of Nicotine.*

**Methyl-Nicotine.** $C^{10}H^{12}(CH^3)^2N^2$.—Prepared by mixing nicotine with iodide of methyl. The reaction proceeds slowly in the cold, but is greatly assisted by heat. The crystalline product of the reaction is to be recrystallised from water. The aqueous solution mixed with recently precipitated oxide of silver yields iodide of silver and solution of methyl-nicotine. The solution evaporated over sulphuric acid at 100° yields a viscid mass containing methyl-nicotine.

Methyl-nicotine is soluble in water, yielding a bitter alkaline solution which feels slippery between the fingers. The solution saturates acids, forming salts of which the sulphate, hydrochlorate, nitrate and hydrocyanate crystallise, but with difficulty (Stahlschmidt). The hydrofluate, acetate, oxalate and tartrate do not crystallise. The alkaline solution described above precipitates salts of iron and copper; it also dissolves recently precipitated hydrate of aluminium. (Stahlschmidt.)

*Hydriodate of Methyl-nicotine,* $C^{12}H^{18}N^2.2HI$. The atom of nicotine unquestionably containing 10 atoms of carbon ($C = 12$), we may assume that it reacts upon 2 atoms of iodide of methyl, so that the resulting compound has the above formula. It is prepared by the action of iodide of methyl on nicotine as above. (Stahlschmidt.)

The *platinum-salt of methyl-nicotine,* $C^{12}H^{18}N^2.2HCl.2PtCl^2$ is a crystalline powder, sparingly soluble in cold water, insoluble in alcohol.—The *gold-salt*, $C^{12}H^{18}N^2.2HCl.2AuCl^3$, is a pale yellow precipitate, almost insoluble in cold water and alcohol.

ETHYL-NICOTINE. The hydrate of this base is prepared by a similar process to the hydrate of methyl-nicotine, substituting iodide of ethyl for iodide of methyl. Its properties are similar to those of methyl-nicotine.

*Hydriodate of Ethyl-nicotine*, $C^{14}H^{22}N^2.2HI$, obtained by the action of iodide of ethyl on nicotine in sealed tubes at 100°, forms fine colourless prisms, very soluble in water, sparingly in alcohol and ether (Von Planta and Kekulé).—The *platinum-salt*, $C^{14}H^{22}N^2.2HCl.2PtCl^2$, is a yellow flocculent precipitate which gradually becomes orange coloured and crystalline.—The *gold salt*, $C^{14}H^{22}N^2.2HCl.2AuCl^3$, is a sulphur-yellow precipitate produced by adding solution of trichloride of gold to a solution of hydrochlorate of ethyl-nicotine; it is soluble in boiling water and is deposited in beautiful needles on cooling.

AMYL-NICOTINE. Known only in solution and in the state of platinum-salt. It is prepared in the same manner as the corresponding compounds of methyl and ethyl, only as iodide of amyl acts sluggishly, the tubes must be heated for some days.

The *platinum-salt*, $C^{20}H^{34}N^2.2HCl.2PtCl^2$, is a yellow precipitate not yet obtained in the crystalline state. C. G. W.

**NIGELLIN.** A viscous substance obtained from *Nigella sativa.* (Reinsch, Pharm. Centr., 1842, p. 314.)

**NIGRIC ACID.** This name was applied by Löwig and Weidmann to a black humus-like substance found among the products of the action of potassium or sodium on oxalic ether. They assigned to it the formula $C^7H^8O^4$. (Handw. d. Chem. v. 573.)

**NIGRIN.** A mixture of rutile with titaniferous iron, occurring in brown-black granules in the gold-sand of Ohlafian in Transylvania; also in crystals having the form of rutile at Bernau in Bavaria. (*Rammelsberg's Mineralchemie*, p. 1008.)

**NIHILUM ALBUM.** An impure oxide of zinc which collects on the sides of the furnaces in the smelting of zinc-ores and the preparation of brass.

**NINAPHTASE, NINAPHTESE, NINAPHTISE.** Laurent's names for moni-, di-, and tri-nitronaphthalene.

**NINAPHTHYLAMINE.** *Ninaphthylidine*, $C^{10}H^8N^2O$ (C. S. Wood, Chem. Gaz. 1859, p. 218).—An organic base produced by passing sulphydric acid gas through a boiling alcoholic and feebly ammoniacal solution of dinitronaphthalene:

$$C^{10}H^6(NO^2)^2 \ + \ 4H^2S \ = \ C^{10}H^8N^2O \ + \ 3H^2O \ + \ S^4.$$

The passage of the gas is continued for about three hours, by which time the greater part of the alcohol has distilled off. The residue is then supersaturated with dilute sulphuric acid, heated to boiling, and filtered. The filtrate on cooling deposits sulphate of ninaphthylamine, from the solution of which the base may be precipitated by ammonia.

Ninaphthylamine crystallises in beautiful carmine-red needles, slightly decomposed at 100°. The *hydrochlorate*, $C^{10}H^8N^2O.HCl$, forms acicular crystals; the *chloroplatinate*, $C^{10}H^8N^2O.HCl.PtCl^2$, is precipitated in yellowish-brown, rather soluble crystals, on adding platinic chloride to a solution of the base in ether-alcohol. The *sulphate* $(C^{10}H^8N^2O)^2.H^2SO^4$, crystallises in white scales, but is decomposed by recrystallisation from its aqueous solution.

**NIOBITE,** or *Columbite.* Native niobite of iron and manganese (p. 54).

**NIOBIUM.** Syn. *Columbium.* Symbol, Nb.—Atomic weight, 98.

A metal discovered in 1801 by Hatchett, in a black mineral called *columbite* from North America, and thence called *Columbium.* Wollaston in 1809 examined it further and pronounced it to be identical with the tantalum discovered by Ekeberg, in Swedish tantalite. This idea of the identity of the two metals remained current till 1846, when H. Rose (Pogg. Ann. lxiii. 317; lxix. 115), by a more careful investigation, was led to conclude that the American columbite and the tantalite from Bodenmais in Bavaria contained two acids bearing a very close resemblance to tantalic acid, but nevertheless distinct from it and from each other. To the metals supposed to exist in these acids, Rose assigned the names *Niobium* and *Pelopium.* But by later investigations (Pogg. Ann. xc. 456) he finds that these two acids really contain the same metal associated with different quantities of oxygen; he therefore discards the name pelopium, and designates the metal contained in American columbite and Bavarian tantalite as niobium. This metal is clearly the same as the one discovered by Hatchett more than sixty years ago, and ought perhaps, in justice to its discoverer, to retain the name *columbium* which he gave to it; but as the rediscovery of the metal is certainly due to Rose, who has moreover completed its chemical history by the preparation and analysis of a considerable number of its compounds, chemists are, for most part, agreed to designate it by the name which he assigned to it, namely *Niobium*. (See the Memoirs already cited; also Pogg. Ann. civ. 310, 432 and 581; cv. 424; cvi. 143; cvii. 566; cviii. 273 and 465; cxi. 193 and 426; cxii. 468 and 549.—Jahresber. 1858, p. 151; 1859, p. 156; 1860, p. 145.—*Traité complet de Chimie analytique*, par H. Rose; Paris, 1858, 1861; i. 306; ii. 469.)

Niobium occurs, as already mentioned, in columbite, which is a compound of niobous oxide with the protoxides of iron and manganese; also, associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian samarskite, urano-tantalite or yttro-ilmenite, also in pyrochlore, euxenite, and a variety of pitchblende from Satersdälen in Norway.

*Metallic niobium* is obtained by heating fluoride of niobium, or fluoride of niobium and potassium or sodium, with sodium in a covered iron crucible, and washing out the soluble salts with water; also, though impure, by heating niobite of sodium in hydrogen gas containing phosphorus vapour. It is a black powder, of specific gravity 6·27—6·67, which oxidises with incandescence when heated in the air, forming niobous oxide, $Nb^2O^3$. When somewhat strongly heated in *chlorine gas*, it is converted, also with incandescence, into a mixture of niobous and niobic chlorides. The metal prepared by the first method dissolves while still moist in boiling dilute *hydrochloric acid*, with evolution of hydrogen, forming a colourless liquid. *Nitric acid* does not dissolve it, even when heated; *nitro-muriatic* acid less easily than hydrochloric acid. It dissolves in hot *hydrofluoric acid*, with evolution of hydrogen, and in a mixture of *hydrofluoric* and *nitric acids*, even at ordinary temperatures. Strong *sulphuric acid* dissolves it on prolonged heating, forming a brownish liquid, which becomes colourless when largely diluted with water, and yields with ammonia a bulky, somewhat brownish precipitate. The metal is oxidised by fusion with *acid sulphate of potassium*, and the fused mass digested in water leaves niobous oxide. It is gradually converted into niobite of potassium by boiling with *aqueous potash*, more quickly by fusion with *carbonate of potassium*.

Niobium forms two series of compounds, the niobous or hyponiobic compounds in which it is triatomic, *e.g.* niobous chloride $NbCl^3$, niobous oxide $Nb^2O^3$, and the niobic compounds in which it is tetratomic, *e.g.* niobic chloride $NbCl^4$, niobic oxide $NbO^2$. Both the oxides are of electro-negative or chlorous character, uniting with basylous oxides to form salts, viz. the niobites or hyponiobates, and niobates.

It is remarkable, however, that niobic oxide cannot be formed from niobous oxide by direct oxidation, and for these reasons, as well as on account of certain differences in the blowpipe reactions, to be afterwards noticed, Rose regards the niobous and niobic compounds, not as related to one another like different oxides, chlorides, &c., of one and the same metal (the ferrous and ferric compounds for example), but rather as distinct series of compounds containing the same metal in different allotropic modifications. Hence he designates the higher oxide, &c., as compounds of *niobium;* the lower as compounds of *hyponiobium*. But when it is remembered that the two chlorides are convertible one into the other (p. 50), and that by their intervention the higher oxide may be formed from the lower, and moreover that the lower oxide can be formed (though not readily) from the higher, by the action of hydrogen and other reducing agents (p. 53), there appears to be scarcely sufficient reason for regarding the two oxides, &c., of niobium as standing to one another in any peculiar relation different from that of the ferrous and ferric compounds, for example; we shall therefore adhere to the ordinary mode of designation by the terminations *ous* and *ic*. The differences in the blowpipe reactions of the two oxides (which are but slight) are doubtless connected with the difficulty of passing from one state of oxidation to the other, a difficulty which we are not at present able to explain.

**NIOBIUM, BROMIDES OF.** Niobium forms two bromides analogous to the chlorides, and obtained by similar processes. Niobous bromide is yellowish, niobic bromide purple-red; both are apt to retain small quantities of free bromine.

**NIOBIUM, CHLORIDES OF.** These compounds are prepared by the action of chlorine at a red heat on the corresponding oxides mixed with charcoal. Niobous oxide or the mixture of that compound with niobic oxide separated from columbite by processes to be hereafter described, is mixed with starch or sugar, and the mixture completely charred by ignition in a covered crucible. It is then introduced in small pieces into a glass tube which is strongly heated by a charcoal fire or a gas furnace, while a stream of dry carbonic anhydride is passed through it. As soon as all the moisture is expelled, the tube is left to cool, the stream of carbonic anhydride being still kept up; the carbonic anhydride apparatus is then replaced by a chlorine apparatus; and the tube is again heated, after the carbonic anhydride and atmospheric air have been completely expelled by the chlorine. Two chlorides are thus obtained, viz. *niobous* chloride, white, volatile, but not fusible; and *niobic* chloride, yellow, volatile, easily fusible, and containing a larger proportion of chlorine. It was the formation of these two chlorides which originally led Rose to conclude that certain varieties of tantalite (or rather columbite) contained two distinct metals, niobium and pelopium; but later experiments convinced him that the substance which he then regarded as perfectly pure niobic acid, obtained by the action of water on the white chloride, may, by mixing it with a large excess of charcoal, and gently igniting it in a stream of chlorine gas, with strict attention to the details above given, be completely converted into the yellow chloride, originally called chloride of pelopium; whereas if a smaller quantity of charcoal be used, or if the mixture be too strongly ignited during the action of the chlorine, especially at the commencement, the white and less volatile chloride (originally called chloride of niobium) is obtained as well as the yellow compound.

*Niobous Chloride*, $NbCl^3$. *Chloride of Hyponiobium.*—The white chloride prepared as above, always retains a certain quantity of oxygen: for when heated in sulphydric acid gas, whereby it is converted into a sulphide, it gives off a small quantity of water, together with the hydrochloric acid. But on heating it in vapour of disulphide of carbon, the oxide with which it is mixed is converted into sulphide, while the chloride itself is volatilised in the stream of vapour, and is thus obtained quite free from oxide. This pure niobous chloride was found to contain 47·86 per cent. niobium and 52·14 chlorine, the formula requiring 48·05 niobium, and 51·95 chlorine. The chloride treated with water is converted into niobous acid.

*Niobic Chloride*, $NbCl^4$.—This is the yellow chloride above mentioned. It gave, as the mean of several analyses, 40·77 per cent. niobium and 59·23 chlorine, the formula requiring 40·91 niobium and 59·09 chlorine. (Respecting the vapour-density, see p. 52.) *Water* converts it into niobic oxide. When pure and free from oxygen it does not yield any niobic sulphide by sublimation in vapour of *disulphide of carbon*. With strong *sulphuric acid*, it gives off hydrochloric acid, and forms a solution which becomes turbid on boiling and solidifies in a jelly on cooling. It dissolves in *hydrochloric acid*, and with aid of heat in aqueous *potash*. With *alcohol* it forms a clear solution, which when freed by distillation from alcohol, hydrochloric acid, and chloride of ethyl, leaves a thick syrupy liquid consisting of niobate of ethyl. *Zinc* immersed in the hydrochloric solution of niobic chloride, diluted with water, produces a fine blue coloration; a still finer colour is obtained by pouring sulphuric acid on niobous chloride, then adding water and metallic zinc.

**NIOBIUM, DETECTION AND ESTIMATION OF.** 1. *Reactions.*—The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. Indeed these two metals may be said to form a group apart, distinguished by marked characters from all others, especially by the perfect insolubility of their oxides in acids after ignition, and by their blowpipe reactions; further by the fact that when fused with excess of acid sulphate of potassium, they dissolve, forming a fused mass from which the oxide of niobium or of tantalum may be completely separated in the insoluble state by dissolving out the soluble salts with water; from silica, which resembles these oxides in its insolubility in acids after ignition, they are easily distinguished by their blowpipe reactions.

Niobous oxide heated before the blowpipe, especially in the inner flame, assumes a greenish-yellow colour while hot, but becomes colourless on cooling. With *borax* it forms in the outer flame a colourless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or *flaming*. In the inner flame the bead assumes a greyish-blue colour, provided it contains a sufficient quantity of the oxide to produce opacity on cooling. In *microcosmic salt*, niobous oxide dissolves in large quantity, forming a colourless bead in the outer flame, and in the inner, a violet coloured, or if the bead is saturated with the oxide, a beautiful blue bead, the colour disappearing in the outer flame. The addition of ferrous sulphate changes the colour to blood-red.

The blowpipe characters of niobic oxide are similar to those of niobous oxide, but not quite identical. When heated alone, it assumes a greyish tint, becoming white again on cooling. The colourless bead formed with *borax* in the outer flame does not become coloured in the inner. The bead formed with *microcosmic salt* has a light brown colour tinged with violet in the inner flame, and becomes colourless in the outer. The addition of ferrous sulphate changes the brown colour to crimson.

Most of the compounds of niobium hitherto discovered in natural minerals are salts of niobous acid. The niobites bear a close resemblance to the tantalates, but are distinguished: 1. By the very different densities of the oxides or anhydrides obtained from them, tantalic oxide having a density of 7—8·26, whereas that of niobous oxide is only 5·5—6·7.—2. By the behaviour of these oxides before the blowpipe, tantalic oxide exhibiting nearly the same characters as niobic oxide.—3. By the behaviour of the solutions of the alkaline niobites and tantalates with hydrochloric acid at ordinary temperatures, the precipitated niobous oxide being insoluble in excess of that acid, whereas the tantalic oxide precipitated from the tantalates dissolves in excess of hydrochloric acid, forming a slightly opaline liquid.—4. The residue left on evaporating the solutions of the alkaline niobites may be heated (but not calcined) without giving rise to the separation of acid salts insoluble in the alkaline liquid, whereas with the tantalates a very considerable portion of the salt is separated in this insoluble condition.—5. The solutions of the alkaline niobites are further distinguished from the tantalates by their behaviour with chloride of ammonium, ferrocyanide of potassium, infusion of galls, and metallic zinc.—6. Niobous oxide is also distinguished from tantalic oxide by the facility with which it is decomposed by ammonia-gas, and sulphydric acid gas.

Niobic oxide is intermediate in its properties between niobous oxide and tantalic oxide, but resembles the latter more than the former. It is distinguished from tantalic oxide by its lower specific gravity, by its behaviour before the blowpipe, especially with microcosmic salt, with which tantalic oxide produces a colourless bead in the inner as well as in the outer flame; and by its behaviour at high temperatures with hydrogen, sulphydric acid, and ammonia-gas, by all of which it is more or less blackened, whereas the same reagents do not affect tantalic oxide. The characters of the alkaline niobates in solution are likewise intermediate between those of the niobites and tantalates, approaching however more nearly to the latter. The most characteristic distinctions between the three classes of salts in solution are afforded by their reactions with hydrochloric acid, sal-ammoniac, ferrocyanide of potassium, and infusion of galls, the last three reagents being added to acid solutions (see also pp. 53, 56).

| | *Niobites.* | *Niobates.* | *Tantalates.* |
|---|---|---|---|
| Hydrochloric acid. | White precipitate insoluble in excess. | White precipitate soluble in excess on boiling. | White precipitate soluble in excess. |
| Chloride of ammonium. | Precipitation slow and incomplete. | Precipitation slow and incomplete. | Complete precipitation as acid tantalate of ammonium. |
| Ferrocyanide of potassium. | Red precipitate. | Brown-red precipitate. | Yellow precipitate. |
| Ferricyanide of potassium. | Bright yellow precipitate. | White precipitate. | White precipitate. |
| Infusion of galls. | Orange-red precipitate. | Orange-yellow precipitate. | Light yellow precipitate. |

2. *Estimation and Separation.*—Most of the compounds of niobium occurring in nature are niobites. They are partially decomposed by heating with strong sulphuric acid, and completely by fusion with caustic alkalis or by long-continued fusion at a very high temperature with alkaline carbonates. A better method, however, is to fuse the levigated mineral in a platinum crucible with six or eight times its weight of acid sulphate of potassium, pulverise the mass when cold, and boil it repeatedly with fresh quantities of water till no more sulphate of potassium, iron, or manganese is dissolved out of it. The residue, which consists of hydrated niobous acid mixed with ferric oxide, stannic acid, and tungstic acid, is then digested in sulphide of ammonium containing excess of sulphur, which removes the stannic and tungstic acids, and converts the iron into sulphide; the liquid is filtered, and the niobous acid washed with water containing sulphide of ammonium, then boiled with strong hydrochloric acid to remove iron, manganese, uranium, cerium, copper, &c., and finally washed with boiling water. The hydrated niobous acid thus prepared is converted into the anhydride by ignition. The anhydride, $Nb^2O^3$, contains 80·33 per cent. niobium.

Some columbites contain titanic acid. To separate this, the mineral is fused with about twelve times its weight of acid sulphate of potassium, and the fused mass is treated with cold water. Acid sulphate of titanium then dissolves, while the sulphate of niobium remain undissolved. The residue is then washed with water, but to obtain complete separation, it is necessary to repeat this treatment both with this residue and with the titanic acid precipitated from the filtrate by ammonia.

The separation of niobium from tantalum is attended with great difficulty; but they have not hitherto been found in the same minerals. Rose has however given a method of separating them founded on the fact that niobite of sodium dissolves with less difficulty than the tantalate in dilute solutions of hydrate and carbonate of sodium.

From the **alkalis**, niobous acid may be separated, if in solution, by precipitation with sulphuric acid; if in the form of an insoluble compound (as in tyrite), by fusion with sulphate of ammonium.

For further details on the separation of niobium from other elements, see **H. Rose** (*Traité de Chimie analytique*, ii. 469).

*Atomic Weight of Niobium.*—Niobic chloride contains, according to the mean of **Rose's** analyses (Ann. Ch. Pharm. cviii. 232), 40·77 per cent. niobium and 59·23 chlorine, which, supposing the compound to be a tetrachloride, $NbCl^4$, gives for the atomic weight of the metal, $Nb = \frac{40·77 \times 142}{59·23} = 98·24$. This gives for the vapour-density of niobic chloride, the number 8·4 ($= \frac{98·24 + 4 . 35·5}{2} \times 0·0693$); but according to Deville's determination (iii. 997), the observed vapour-density of this compound is much higher, viz. 10·9, which does not differ much from the theoretical density calculated on the supposition that niobic chloride is a pentachloride, $NbCl^5$, and consequently the atomic weight of niobium equal to 114·6: for $\frac{114·6 + 6 . 35·5}{2} \times 0·0693 = 10·1$. The atomic weight of niobium and the formulæ of its compounds must then for the present be considered as somewhat doubtful; still, from the close resemblance in properties between the niobic and tantalic compounds, it is most probable that they likewise correspond in composition, and therefore that the true formula of niobic chloride is $NbCl^4$.

**NIOBIUM, FLUORIDES OF.** *a. Niobous fluoride* or *Fluoride of Hyponiobium.* $NbF^3$.—Hydrated niobous oxide dissolves in strong hydrofluoric acid even at ordinary temperatures, forming a solution which does not yield any crystals, but leaves on evaporation a mass which, when more strongly heated, gives off white fumes of the fluoride and leaves niobous oxide. When ignited niobous oxide is mixed with hydrofluoric acid in a platinum-retort and then strong sulphuric acid added, vapours of niobous fluoride are given off without external heating; on applying heat, the niobous fluoride is decomposed by the sulphuric acid, and nothing but hydrofluoric acid passes over.

Niobous fluoride unites with the fluorides of the alkali-metals, forming the salts $2KF.NbF^3$ (usually mixed with fluoride of potassium) and $NaF.NbF^3$ (always mixed or combined with acid fluoride of sodium). These double fluorides are soluble in water, forming acid solutions which when mixed with sulphuric acid and concentrated till that acid begins to evaporate, yield a deposit of niobous acid.

*β. Niobic Fluoride.* $NbF^4$.—Hydrated niobic oxide dissolves easily in aqueous hydrofluoric acid, and the solution forms crystallisable double salts with metallic fluorides and with hydrofluoric acid. On adding carbonate of potassium to a solution of niobic acid in excess of hydrofluoric acid, a bulky precipitate is formed at first, but redissolves when the liquid is completely neutralised, the solution as it cools depositing the salt $2KF.NbF^4$; and the mother-liquor when evaporated yields the salt $8KF.3NbF^4$ (perhaps a mixture of the preceding with fluoride of potassium), afterwards on further evaporation, hydrated fluoride of potassium. A solution of niobic acid in hydrofluoric acid only partially neutralised with potash, and evaporated to the crystallising point, yields the salt $K^2NbF^6.2KHF^2$. With soda in like manner the salt $Na^4NbF^8.2NaHF^2$ is obtained as a crystalline precipitate; the liquid filtered therefrom yields on standing, the salt $Na^2NbF^6.2NaHF^2$; and the mother-liquor separated from this, deposits the salt $Na^2NbF^6$ or $2NaF.NbF^4$.

The solutions of the double niobic fluorides are not clouded by sulphuric acid, and in order to convert the niobic fluoride into niobic acid, they must be evaporated with excess of sulphuric acid.

**NIOBIUM, NITRIDES OF.** *a.* A nitride of niobium is obtained by heating niobic chloride in ammonia-gas. When freed by water from admixed chloride of ammonium, it forms a dull black powder which conducts electricity, is not attacked by nitric acid, scarcely by nitromuriatic acid, but easily by a mixture of nitric and hydrofluoric acids. The same compound is formed, though in a less pure state, by passing ammonia-gas over strongly ignited niobic oxide. Niobic oxide heated in cyanogen gas yields a similar black compound containing carbon as well as nitrogen, but in much too small a proportion to form a cyanide.

*β.* Another nitride of niobium (Rose's nitride of hyponiobium) is obtained in like manner from niobous chloride or oxide. Its properties are similar to those of the preceding. Both compounds give off large quantities of ammonia when fused with hydrate of potassium.

**NIOBIUM, OXIDES OF.** Niobium forms two oxides analogous in composition

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to the chlorides, and formed from them by the action of water. Both of them form salts with basic metallic oxides.

α. **Niobous Oxide or Anhydride.** $Nb^2O^3$. (Rose's *Oxide of Hyponiobium.*) In the hydrated state, *Niobous acid*. This oxide may be prepared in several ways:—1. By decomposing niobous chloride, $NbCl^3$, with water:

$$2NbCl^3 + 3H^2O = Nb^2O^3 + 6HCl.$$

2. By fusing columbite or other minerals containing it with acid sulphate of potassium and treating the fused mass with water &c. as described in speaking of the estimation of niobium in these minerals (p. 51). The purest niobous oxide is obtained from the columbite of Bavaria and of North America; that obtained from samarskite, euxenite, fergusonite, tyrite, &c., is more difficult to purify, on account of the presence of other acid oxides, those of titanium and zirconium, for example.—3. By the reduction of niobic oxide. This reduction cannot however be effected completely; the most effectual reducing agent is acid sulphate of ammonium, which when fused with niobic oxide, reduces about a third of it to niobous oxide; other ammoniacal salts act less powerfully or not at all; sulphide of ammonium exerts no reducing action; that of cyanide of potassium is uncertain.

Niobous oxide is white, but becomes yellow when heated, the colour disappearing again on cooling. Its specific gravity varies according to the degree of heat to which it has been exposed in preparation. The oxide prepared directly from columbite by fusion with acid sulphate of potassium has the highest specific gravity, viz. 5·208 to 6·13 and even 6·54; that prepared by the action of water on the chloride is a hydrate (niobous acid); it is amorphous and has a density of 5·25; but by exposing the niobous chloride to moist air, so that it may be slowly decomposed, a crystalline hydrate is formed having a density of 4·6—4·7. By exposing the amorphous hydrate to a red heat for a long time, or to a white heat for a shorter time, it is converted into anhydrous niobous oxide having nearly the same density as the crystalline hydrate. At the highest temperature of a porcelain furnace, the oxide is converted into a sandy powder consisting of microscopic crystals, of specific gravity 4·00; in one experiment it was fused at this high temperature, and formed on cooling a radio-crystalline mass.

The hydrate prepared by the action of water on the chloride, and likewise that precipitated by hydrochloric acid from solutions of alkaline niobites, exhibits bright incandescence when calcined; the oxide containing sulphuric acid obtained by fusing columbite with acid sulphate of potassium does not exhibit this phenomenon.

Niobous oxide heated in *hydrogen gas* turns grey and is partially reduced; but the loss of weight does not exceed 1 per cent. (tantalic oxide suffers no reduction). Niobous oxide is decomposed by ignition in a stream of *sulphydric acid gas*, or vapour of *sulphide of carbon*, being converted into niobous sulphide. Ignited in *ammonia gas* it turns black, gives off a large quantity of water, and is partly converted into a nitride (p. 52).

Niobous oxide after ignition is insoluble in all acids. The hydrate dissolves with difficulty in *hydrochloric acid*, so that when an alkaline niobite is precipitated by an excess of hydrochloric acid, the filtrate retains only a small quantity of niobous acid in solution; but on boiling for some time with strong hydrochloric acid, and then adding water, a considerable quantity will be dissolved, and by repeating this treatment with acid and water two or three times on the residue, the whole may be ultimately dissolved. The hydrate dissolves easily in *hydrofluoric acid*, but is nearly insoluble in *nitric acid*.

NIOBITES.—Niobous oxide unites with basic metallic oxides forming definite salts, several of which occur as natural minerals. The niobites of the alkali-metals are either mono- or trimetallic, $MNbO^2$ or $M^3NbO^3$: those of the earth-metals and heavy metals are monometallic, $M'NbO^2$ or $M''Nb^2O^4$. The niobites of the alkali-metals are produced by fusing niobous oxide with the hydrates of those metals or by boiling niobous acid with solutions of caustic alkalis.

The alkaline niobites are likewise soluble in solutions of potash and carbonate of potassium, but dissolve with great difficulty in excess of soda and carbonate of sodium. Niobous acid is precipitated from its alkaline solutions by acids, especially by *sulphuric acid*, even at ordinary temperatures (the precipitation of tantalic acid requires the aid of heat). Oxalic acid does not affect alkaline niobites; but *carbonic acid* gas precipitates an acid salt soluble in a large quantity of water; *acetic acid* and *sal-ammoniac* also form precipitates, but the precipitation by the latter is slow and imperfect, especially if the solution contains carbonate of potassium or sodium. A solution of an alkaline niobite, acidulated with sulphuric or hydrochloric acid, forms a red precipitate with *ferrocyanide of potassium*, bright yellow with the *ferricyanide*, and orange-red with *infusion of galls*. A piece of *zinc*, immersed in the acidulated solution, forms a

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beautiful blue precipitate, which after a while changes to brown. Tantalates yield only a faint blue colour with zinc, on addition of a very large quantity of hydrochloric acid.

*Niobites of Potassium.* The *monopotassic* salt is difficult to obtain in definite forms, being soluble in excess of hydrate and carbonate of potassium. When niobous oxide is fused with carbonate of potassium, a quantity of carbonic anhydride is expelled corresponding to the formation of the *tripotassic* salt, $K^3NbO^3$.

*Niobites of Sodium.* The *monosodic salt*, $NaNbO^2$ or $Na^2O.Nb^2O^3$, crystallises with 2 proportions of water, viz. $2NaNbO^2.5H^2O$ and $2NaNbO^2.7H^2O$. It gives off the greater part of its water of crystallisation at 100°, but still remains completely soluble in water; by ignition it is resolved into an acid salt and caustic soda. It is insoluble in strong solutions of hydrate and carbonate of sodium; but dilute soda-solutions take it up more readily than niobate or tantalate of sodium, so that niobic acid and tantalic acids are most easily separated from niobic acid by digestion in solutions of hydrate or carbonate of sodium of a certain degree of dilution.

By fusing niobous oxide with carbonate of sodium, a basic salt is obtained together with acid salts partially soluble in water; by continuing the fusion till no further loss of weight is sustained, the *trisodic salt*, $Na^3NbO^3$, is produced; it is resolved by water into the monosodic salt and free soda. Carbonic anhydride passed into the solution of niobite of sodium gradually throws down an acid salt.

A very *acid niobite of ammonium* separates after some time from a solution of niobite of sodium mixed with chloride of ammonium.

A solution of monosodic niobite added to excess of the solutions of neutral salts of the earth-metals and heavy metals, forms precipitates having the general formula $M'NbO^2$ or $M''Nb^2O^4 = M''O.Nb^2O^3$.

*Niobite of Iron and Manganese.* (FfeO; MmnO). $Nb^2O^3 = \left.\begin{matrix} \overset{'''}{Nb^2} \\ (Ffe\,;\,Mmn)'' \end{matrix}\right\} O^4$.

*Columbite. Niobite.*—This is the mineral in which niobium or columbium was first discovered. It occurs in trimetric prisms, exhibiting the combination $\infty\bar{P}\infty$ . $\infty\breve{P}\infty$ . oP . $\infty P$ . $\infty\bar{P}2$ . $\infty\breve{P}3$ . $\frac{1}{2}\bar{P}\infty$ . $\bar{P}3$ . P, with other faces. Axes $a : b : c = 0·8292 : 1 : 0·8773$. Angles $\infty P : \infty P = 100° 40'$; $oP : \bar{P}\infty = 133° 22·5'$ (Dana, ii. 353). A crystal of columbite from the granite of Monte Video examined by Maskelyne (Phil. Mag. [4] xxv. 41), exhibited the combination $\infty\bar{P}\infty$ . $\infty\breve{P}\infty$ . oP . $2\breve{P}2$ . $\infty P$ . $\infty\breve{P}3$ . $\infty\breve{P}5$, with the angles $\infty\breve{P}\infty : \infty\breve{P}5 = 153° 40'$; $\infty\breve{P}3 : \infty\breve{P}5 = 166° 42'$. Columbite also forms twins, with face of composition parallel to $2\bar{P}\infty$. Cleavage parallel to $\infty\bar{P}\infty$ and $\infty\breve{P}\infty$, the latter the most distinct. It occurs also massive, but rarely. Hardness = 6. Sp. gr. = 5·4—6·4; 5·469 for the Connecticut mineral; 5·7—6·39 for the Bavarian. Lustre submetallic. Colour, various shades of black, often iridescent. Streak dark red to black. Fracture subconchoïdal, uneven. Brittle. It is not altered by heat alone. By *borax* before the blowpipe it is slowly dissolved, giving the reactions of iron and manganese; the bead, if saturated to a certain extent, may be rendered greyish-white by flaming, especially if it has been previously heated in the inner flame; if fully saturated, it becomes opaque spontaneously on cooling. With *carbonate of sodium* it gives the manganese reaction. Many columbites heated on charcoal with soda and borax in a strong reducing flame, yield metallic tin.

*Analyses of Columbite.*

| | Bavaria. | | Connecticut. | | Chanteloub. | Fioland. | Ilmen mountains. | |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* |
| Specific gravity | 6·390 | 6·078 | 5·80 | 6·03-6·05 | 5·6-5·7 | | 5·43-5·73 | 5·45 |
| Niobous oxide ($Nb^2O^3$) | 81·07 | 80·64 | 78·22 | 79·80 | 78·74 | 82·5 | 80·47 | 76·66 |
| Stannic oxide ($SnO^2$) | 0·45 | 0·10 | 0·40 | 0·56 | . . | 1·0 | . . | 0·42 |
| Tungstic oxide ($WO^3$) | . . | . . | 0·26 | | | trace | | |
| Ferrous oxide | 14·30 | 15·33 | 14·06 | 15·00 | 14·50 | 13·2 | 8·50 | 14·29 |
| Manganous oxide | 3·85 | 4·65 | 5·63 | 4·50 | 7·17 | 5·5 | 6·09 | 7·55 |
| Cupric oxide | 0·13 | | | | | | | |
| Uranous oxide | . . | . . | . . | . . | . . | . . | 0·50 | 0·54 |
| Lime | . . | 0·21 | . . | . . | . . | . . | . . | 0·54 |
| Magnesia | . . | . . | 0·49 | . . | . . | . . | 2·44 | |
| Yttria | . . | . . | . . | . . | . . | . . | 2·00 | |
| | 99·80 | 100·93 | 99·06 | 99·86 | 100·41 | 102·2 | 100·00 | 100·00 |

*a.* From Bodenmais in Bavaria (H. Rose).—*b.* From the same (Awdejew).—*c.* From Middletown, in Connecticut (Hermann).—*d.* From the same (Oesten).—*e.* From Chanteloub, Limoges (Damour). *f.* From Hermankär near Bjorkskär, in Finland (Nordenskiöld).—*g.* From the Ilmen mountains near Miask in the Ural (Hermann).—*h.* From the same (Oesten), *Rammelsberg's Mineralchemie*, p. 393.

The columbite of Bodenmais, on the Rabenstein, near Zwiesel, occurs in granite. In the United States it occurs both in felspathic and in albitic granite.

*Niobites of Yttrium.* To this head belong the minerals *Fergusonite*, *Tyrite*, and *Bragite*, which are in all probability identical. Fergusonite has been already described (ii. 623). Tyrite occurs near Arendal in Norway, in crystals too small for measurement, but probably quadratic, exhibiting distinct cleavage and having a density of 5·13 to 5·56. According to Bondi and Kenngott, their form is identical with that of Fergusonite. The mineral decrepitates and gives off water when heated, and exhibits with fluxes the reactions of iron and uranium.

*Bragite*, also from Arendal, has a grey-brown colour, metallic lustre, uneven small splintery fracture; hardness = 45; sp. gr. = 5·40.

The following are analyses of these minerals; that of fergusonite has been already given, but is repeated here for the sake of ready comparison.

| | Tyrite. | | | Bragite. | Fergusonite. | |
|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
| Niobous oxide | 44·90 | 44·48 | 43·49 | 48·10 | 47·75 | 48·84 |
| Stannic " | . . | . . | 0·09 | . . | 1·00 | 0·35 |
| Zirconic " | . . | 2·78 | 0·80 | 1·45 | 3·02 | 6·93 |
| Alumina | 5·66 | 3·55 | 1·35WO$^3$ | | | |
| Yttria | 29·72 | 27·83 | 31·90 | 32·71 | 41·91 | 38·61 |
| Cerous oxide | 5·35 | 5·63 | 3·68 | 7·43 | 4·68 | 3·05 |
| Oxide of lanthanum | . . | 1·47 | . . | | | |
| Uranous oxide | 3·03 | 5·99 | 4·12 | 4·95 | 0·95 | 0·35 |
| Ferrous oxide | 6·20 | 2·11 | 1·12 | 1·37 | 0·31 | 1·33 |
| Manganous oxide | . . | . . | . . | 0·11 | | |
| Protoxide of lead | . . | . . | 0·41 | 0·09 | | |
| Lime | 0·81 | 1·68 | 1·95 | 1·82 | | |
| Potash | . . | . . | 7·23 | 0·39Mg$^2$O | | |
| Water | 4·52 | 4·66 | 3·71 | 1·03 | | |
| | 100·19 | 100·18 | 99·85 | 99·45 | 99·62 | 99·46 |

*a, b, c.* Forbes (Phil. Mag.' [4] xiii. 91).—*d.* Michaelson (J. pr. Chem. xc. 108).—*e.* Hartwall (Pogg. Ann. xvi. 479).—*f.* Weber, *Inaugural dissertation*, Berlin, 1859, p. 59.

The composition of these minerals may be represented by the general formula,

$$3M''O.Nb^2O^3.H^2O \text{ or } \left.\begin{matrix} \overset{'''}{Nb}{}^2 \\ \overset{''}{M}{}^3 \end{matrix}\right\} O^6.H^2O.$$

*Uranoniobite of yttrium and Iron.* *Samarskite*, *Uranotantalite*, M"O(Nb; U)$^2$O$^3$. Trimetric. Angle of prism $2\bar{P}\infty$ = 135° to 136°, therefore $\infty P : \infty P$ = 100° 40′ to 101° 40′, which is near that of columbite. Occurs generally in flattened grains. Hardness = 5·5—6. Specific gravity = 5·614—5·68. Lustre of fracture-surface shining and submetallic. Colour velvet-black. Streak dark reddish-brown. Opaque. Fracture subconchoïdal. When heated, it decrepitates slightly, glows and becomes blackish-brown. Before the blow-pipe it melts on the edges to a black glass. With *borax*, in the outer flame, it forms a yellowish-green to reddish glass; in the inner a yellow to greenish-black glass, which becomes opaque and yellowish-brown by flaming. With *microcosmic salt*, an emerald-green bead in both flames. With *carbonate of sodium*, the reaction of manganese. When pulverised it is slowly but completely decomposed by hydrochloric acid, forming a greenish liquid; more easily by sulphuric acid.

*Analyses of Samarskite.*

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* |
|---|---|---|---|---|---|---|---|
| Niobous oxide | 56·38 | 56·00 | 55·91 | 55·10 | 56·36 | 47·47 | 50·17 |
| Tungstic " | | | | 0·48 | | 1·36 | |
| Zirconic " | . . | . . | . . | . . | . . | 4·35 | 4·25 |
| Stannic " | . . | . . | . . | 0·26 | . . | 0·05 | 0·63 |
| Uranic " | 14·16 | 16·70 | 16·77 | 19·22 | 16·63U$^2$O | 11·60 | 11·08 |
| Ferrous " | 15·43 | 15·90 | 15·94 | 15·05 | 8·87 | 11·08 | 10·55 |
| Manganous " | . . | . . | . . | 0·56 | 1·20 | 0·96 | 1·61 |
| Cupric " | . . | . . | . . | 0·07 | . . | 0·25 | |
| Cerous " | . . | . . | . . | . . | 2·85 | 3·31 | 15·90 |
| Yttria | 9·15 | 11·04 | 8·36 | 4·91 | 13·29 | 12·61 | |
| Thorina | . . | . . | . . | . . | . . | 6·05 | 5·55 |
| Lime | 0·92 | 1·02 | 1·88 | 0·44 | . . | 0·73 | 0·64 |
| Magnesia | 0·80 | 0·75 | 0·75 | 0·26 | 0·50 | 0·14 | 0·04 |
| Water | . . | . . | . . | . . | 0·33 | 0·45 | 0·40 |
| | 96·84 | 101·41 | 99·61 | 96·35 | 100·03 | 100·41 | 100·82 |

*a, b, c,* by Peres; *d.* by Chandler, under H. Rose's direction (Pogg. Ann. lxxi. 157; lxxii. 469; lxxiii. 449).—*e.* by Hermann (J. pr. Chem. l. 178)—*f.* by Finkener; *g.* by Stephens, under Rose's direction (Pogg. Ann. cxviii. 339, 406, 497. Bull. Soc. Chim. v. 491; Jahresb. 1863, p. 829).

The formula of samarskite is that of columbite with part of the niobium replaced by uranium.

Samarskite is from the Ilmen mountains near Miask, where it occurs with æschynite in reddish-brown felspar.

Hermann's *yttro-ilmenite*, a mineral from the same locality, agreeing with samarskite in crystalline form and density, but supposed by him to contain a peculiar acid, ilmenic acid (iii. 245) is, according to H. Rose, nothing but samarskite containing a small quantity of tungstic acid.

**Niobic Oxide or Anhydride,** $NbO^2$. In the hydrated state, *Niobic acid.*—This oxide occurs in combination with lime and other bases in pyrochlore and in euxenite (ii. 611), and is produced artificially in the form of a hydrate by the action of water on niobic chloride; in the anhydrous state by roasting niobic sulphide nitride of niobium. It has not hitherto been obtained by direct oxidation of niobous oxide.

Niobic oxide is white at ordinary temperatures, yellow while hot. Like niobous oxide, it varies in density according to the mode of preparation and the heat to which it has been exposed. The hydrate prepared from the chloride is amorphous or crystalline according as that compound has been decomposed quickly by water, or slowly by exposure to moist air; in the latter case its density is usually 6·2; the oxide prepared by fusion with acid sulphate of potassium has about the same density. By exposing either of the products for a considerable time to a white heat, their density is diminished to about 5·7. The hydrate glows when heated, and is converted into the anhydrous oxide, glassy or crystalline according as it has been obtained from the amorphous or the crystalline hydrate. Niobic acid prepared by treating the chloride with water is not quite insoluble in hydrochloric acid.

NIOBATES. Niobic oxide unites with bases in several proportions. Rose regards as neutral the salts containing $M^2O.2NbO^2 = M^2Nb^2O^5$, or in the case of diatomic metals, $M''Nb^2O^5$. The niobates of the alkali metals are soluble in water, and their solutions yield with *hydrochloric acid* a precipitate of niobic acid, the precipitation being complete if it takes place in the cold and the hydrochloric acid is not added in too great excess; if, however, the alkaline niobate is boiled with a large excess of hydrochloric acid, a turbid liquid is formed which becomes clear on dilution with water, and from the solution thus formed, the niobic acid is precipitated by sulphuric acid only when the quantity of hydrochloric acid present is below a certain limit. *Nitric acid* reacts with solutions of alkaline niobates in the same manner as hydrochloric acid. *Phosphoric, arsenic, oxalic, tartaric, racemic,* and *citric acids* form no precipitate in these solutions; *acetic acid*, on the contrary, precipitates them; *hydrocyanic acid* merely renders them opalescent; *Gallic* and *tannic acids* (or infusion of galls) produce no precipitate unless the solution is acidulated with hydrochloric or sulphuric acid, in which case an orange-yellow precipitate is formed. If the greater part of the niobic acid be thrown down from the solution of an alkaline niobate by hydrochloric acid, and metallic *zinc* then introduced, the niobic acid becomes first blue, then brown, and after some time white again; if dilute *sulphuric acid* be used instead of hydrochloric, the blue coloration is produced more slowly, but is generally purer; it is best produced by using hydrochloric acid with addition of dilute sulphuric acid. The blue niobic acid turns brown on addition of ammonia, and on exposure to the air quickly becomes white again.

*Niobates of Potassium.*—Monopotassic niobate cannot be obtained pure by fusing niobic anhydride with hydrate of potassium, since it is soluble in hydrate of potassium in all proportions, and cannot be isolated by crystallisation. Niobic anhydride fused with carbonate of potassium expels carbonic anhydride, and forms the compounds $6K^2O.5NbO^2$ and $7K^2O.5Nb^2O^2$; the quantity of carbonic anhydride eliminated increasing with the duration of the fusion.

*Niobates of Sodium.*—When niobic anhydride is added to melting hydrate of sodium, a strong action takes place, attended with incandescence; and on subsequently treating the fused mass with water, the excess of sodium-hydrate is first removed and fresh water then dissolves the so-called *neutral salt*, $Na^2O.2NbO^2$ or $Na^2Nb^2O^5$, which crystallises from the solution generally with 7 at., but sometimes with 5 at. water.

Salts containing a larger proportion of acid are obtained, together with that just mentioned, by fusing niobic anhydride with carbonate of sodium, also, though slowly, by decomposing a solution of the neutral salt with carbonic acid. By fusing together weighed quantities of niobic anhydride and carbonate of sodium, and keeping the heat moderate, a quantity of carbonic anhydride is expelled corresponding to the formation of the salt $Na^2O.NbO^2$ or $Na^2NbO^3$; at higher temperatures, however, a larger quantity of carbonic anhydride is expelled.

*Chloride of ammonium* added to a solution of niobate of sodium forms an immediate precipitate, which however contains but a small quantity of ammonia.

On adding the solution of the sodium-salts to a neutral salt of an earth-metal or a heavy metal, precipitates are formed consisting of neutral niobates having the composition $M^2O.NbO^2$ or $M''NbO^3$. Rose has obtained the magnesium, zinc, silver, mercurous and cupric salts.

*Niobate of Calcium, Cerium, &c.*—This is the composition of pyrochlore, a mineral occurring imbedded in syenite at Fredriksvärn and Lauwig in Norway, associated with zircon, polymignite, and phosphate of yttrium; also at Brevig with thorite; in the Ilmen mountains near Miask, and associated with tourmalin in the albite vein at Chesterfield, Massachusetts. Monometric, occurring in octahedrons modified by faces of the cube, also in dodecahedrons and trapezohedrons 2O2, 3O3. Cleavage octahedral, sometimes distinct, especially in the smaller crystals. Hardness = 5—5·5. Specific gravity = 3·802 from Brevig (Berzelius); 4·32 from Miask (Rose); 4·203 from Miask (Hermann); 4·203—4·221 from Fredriksvärn (Hayes). Lustre vitreous or resinous. Colour pale honey-yellow, brown, dark reddish or blackish-brown. Subtranslucent to opaque. Fracture conchoïdal. Before the blowpipe it becomes pale brownish-yellow or lemon-yellow, but retains its lustre and fuses with great difficulty. With *borax* it yields, in the outer flame, a reddish-yellow transparent glass which becomes opaque by flaming, and with a larger proportion of borax forms a white enamel. In *microcosmic salt* it dissolves completely, forming in the outer flame a yellow glass which becomes grass-green on cooling.

| | Fredriksvärn. | | Brevig. | | Miask. | |
|---|---|---|---|---|---|---|
| | Wöhler. | Hayes. | Wöhler. | Chydenius. | Wöhler. | Hermann. |
| Niobic oxide | 62·75 | 53·10 | 67·02 | 61·07 | 67·37 | 60·83 |
| Titanic oxide | | 20·20 | trace | | | 4·90 |
| Stannic oxide | 0·61 | . . | . . | 0·57 | | |
| Ceric oxide | 6·80 | . . | 5·16 | . . | 13·15 | 15·23* |
| Alumina | . . | . . | | | | |
| Ferric oxide | 2·16 | 2·35 | | | | |
| Uranic oxide | . . | . . | 4·60 | 2·82 | | |
| Uranous oxide | 5·18 | 1·20 | . . | | | |
| Ferrous oxide | . . | . . | 1·33 | | | |
| Manganous oxide | 2·75 | . . | 1·69 | . . | 1·28 | 2·23 |
| Cerous oxide | . . | . . | . . | 5·00 | 0·14 | |
| Yttria | . . | . . | . . | 4·62 | | |
| Thorina | . . | . . | . . | 16·02 | 0·81 | 0·94 |
| Lime | 12·85 | 19·45 | 9·88 | . . | 10·98 | |
| Magnesia | . . | | | . . | | 9·80 |
| Soda | . . | . . | . . | 4·60 | 5·29 | 1·46 |
| Potash | . . | . . | . . | . . | . . | 3·62 |
| Fluorine | trace | . . | . . | not det. | 3·23 | 0·65 |
| Water | 4·20 | 0·80 | 7·06 | 1·17 | 1·16 | 2·21 |
| | 97·30 | 97·10 | 96·74 | 95·87 | 103·41 | 101·87 |

Wöhler (Pogg. Ann. vii. 417; xxvii. 80; xlviii. 83; Ann. Ch. Pharm. lxi. 264). Hayes (Sill. Am. J. xlvi. 158, 164). Chydenius (Jahresb. 1863, p. 83). Hermann (J. pr. Chem. xxxi. 94; l. 189; lxviii. 96). According to Hermann's most recent statement, pyrochlore contains niobous as well as niobic acid.

Pyrochlore (or Microlite) from Chesterfield, Massachusetts, contains, according to Shepard (Sill. Am. J. xxxii. 338), 75·70 per cent. niobic oxide, 7·42 tungstic oxide, uranous oxide and yttria, 14·84 lime, and 2·04 water.

*Euxenite* (ii. 611) from Norway is essentially a titano-niobate of yttrium and uranium.

*Æschynite* (i. 59) from Miask, is, according to Hermann, a compound of titanic and niobic (perhaps also niobous) oxides with ceric, ferric, lanthanic oxide, &c.

*Polycrase*, a mineral from Hitteröe in Norway agreeing in crystalline form with columbite and samarskite, contains, according to Scheerer (Pogg. Ann. lxii. 430; lxxii. 568) and Hermann (J. pr. Chem. l. 181), titanic, niobic and zirconic oxides, combined with ferric oxide, uranic oxide, cerous oxide, and yttria, small quantities of alumina, and traces of lime and magnesia.

**NIOBIUM, SULPHIDES OF.** The compound $Nb^2S^3$ is produced by the action of sulphydric acid gas on niobic chloride, at ordinary or more quickly at higher temperatures, or by passing the vapour of sulphide of carbon mixed with carbonic anhydride (to carry it forward) over strongly ignited niobic oxide. It is a black powder which conducts electricity and acquires metallic lustre by trituration. It is decomposed by chlorine at a gentle heat, yielding niobic chloride and chloride of sulphur.

The same compound is formed by heating niobous chloride in sulphydric acid gas. Niobous oxide is converted by sulphide of carbon vapour at a red heat into the compound $Nb^2S^3.3NbS$, and at a white heat into $Nb^2S^3.7NbS$. These products, called by Rose *sulphide of hyponiobium*, resemble the sulphide, $Nb^2S^3$, in physical properties, excepting that they acquire a steel-grey colour by trituration, whereas $Nb^2S^3$ remains black. By ignition in hydrogen gas they are converted in $Nb^4S^3$. When burnt in the air they yield niobous oxide.

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* With oxide of lanthanum.

**NEPHOLITE.** A variety of chiolite (fluoride of aluminium and sodium, $2NaF.AlF^3$), found at Miask in the Ural. (See Sodium, Fluoride of.)

**NITHIALIN.** A yellow amorphous substance, produced by the action of sulphide of ammonium on paranitraniline. (Arppe, Ann. Ch. Pharm. xcvi. 113.)

**NITRACROL.** A heavy colourless pungent liquid, formed, together with others, by the action of strong nitric acid on œnanthol (Tilley, Phil. Mag. [3] xxxiii. 81); also on choloïdic acid (Redtenbacher, Ann. Ch. Pharm. lvii. 145).

**NITRAMARINE.** See Amarine (i. 162).

**NITRAMIDIN.** An explosive substance produced by the action of strong nitric acid upon starch, also called Xyloïdin (*q. v.*).

**NITRAN.** Graham's name for the radicle $NO^2$, which must be supposed to exist in the nitrates, when they are regarded as formed on the type of the chlorides, *e.g.* nitric acid, $NO^2.H$.

**NITRANIDES.** Syn. with Nitrates.

**NITRANILINE.** See Aniline, Nitric Derivatives of, under Phenylamines.

**NITRANISIC ACIDS.** See Anisic Acid (i. 302).

**NITRANISIDE.** See Anise, Oil of (i. 298).

**NITRANISIDINE.** See Anisidine (i. 304).

**NITRANISOL.** See Anisol (i. 305).

**NITRATES.** See Nitric acid, under Nitrogen, Oxides and Oxygen-Acids of.

**NITRATIN.** Native nitrate of sodium. See Nitrates.

**NITRAZOPHENYLAMINE.** See Aniline, Nitric Derivatives of, under Phenylamines.

**NITRAZOPHENYL-CITRACONAMIC ACID.**
**NITRAZOPHENYL-CITRACONAMIDE.** } See the last reference.

**NITRE.** A name applied sometimes to nitrate of potassium, sometimes to nitrate of sodium, but more frequently in commercial language to the latter, the potassium-salt being more especially distinguished as saltpetre.

**NITRIC ACID.** See Nitrogen, Oxides and Oxygen-Acids of.

**NITRICUM.** Syn. with Nitrogen.

**NITRIDES.** This term might be applied to the compounds of nitrogen with any other element or radicle, but it is chiefly used to designate the compounds of nitrogen with phosphorus, boron, silicon, and the metals. The metallic nitrides have for the most part the composition denoted by the formulæ RN, $R^2N$, or $R^3N$ (R denoting a monatomic metal), the last being analogous to ammonia. They are mostly obtained by the action of ammonia on metallic oxides or chlorides; frequently also by the direct action of atmospheric nitrogen on metals at the moment of separation from their oxides by charcoal. Most of them have a metallic aspect, are easily decomposed by heat, sometimes with explosion; some of them however withstand a very high temperature without decomposition. Many of them are reduced to the metallic state by ignition in hydrogen or ammonia-gas; heated with water or hydrate of potassium; they often yield metallic oxides and ammonia; they burn when heated in the air. They unite with other metallic compounds, especially with metalamides.—[For the special descriptions of these compounds, see the several metals; for the methods of analysing them, see page 65.]

**NITRILES.** This term is applied to the cyanides of the alcohol-radicles regarded as compounds of nitrogen with acid radicles; thus cyanide of ethyl $C^2H^5.CN$ = propionitrile $C^3H^5.N$. (See Cyanides, ii. 202, 211, 258, 272, 274; also Benzonitrile, i. 503, and Cyanide of Cetyl, i. 840.)

Mendius (Ann. Ch. Pharm. cxxi. 129) has shown that the nitriles are converted by direct assumption of hydrogen into amines, according to the general equation: $C^nH^{2n-1} + H^4 = C^nH^{2n+3}N$; *e.g.* formonitrile (cyanide of hydrogen) into methylamine, acetonitrile into ethylamine, &c. The conversion is effected by bringing the nitrile mixed with hydrochloric acid and alcohol into contact with metallic zinc. (See METHYLAMINE, iii. 995.)

**NITRINDIN.** See INDIN (iii. 266).

**NITRITES.** See NITROUS ACID, under NITROGEN, OXIDES and OXYGEN-ACIDS OF.

**NITRAZOBENZENE.** See AZOBENZENE (i. 478).

**NITROBENZAMIDES.** See BENZAMIDE (i. 541).

**NITROBENZANILIDE.** See PHENYL-BENZAMIDE, under PHENYLAMINES.

**NITROBENZANISIDIDE,** or BENZONITRANISIDE (see ANISIDINE, i. 304).

**NITROBENZENES.** See BENZENE (i. 543).—The following are additional modes of formation and transformation of these compounds.

1. Nitrobenzene is produced, together with other products, by the action of strong nitric acid on oil of turpentine (H. Schiff, Ann. Ch. Pharm. cxiv. 201). See TURPENTINE.

2. In preparing nitrobenzene for use in perfumery, H. Vohl recommends that the benzene be first distilled at a temperature below 83°, to free it from a volatile sulphuretted body which it usually contains. The nitrobenzene is subsequently to be distilled in a current of aqueous vapour, and the portion of the product which remains dissolved in the water separated by addition of common salt. (Dingl. pol. J. clxvii. 148.)

3. Nitrobenzene distilled for a long time with chromate of potassium and sulphuric acid, is converted into nitrophenoic acid, $C^6H^3(NO^2)O^2$ (Church, Chem. Soc. Qu. J. xiv. 52). See PHENOIC ACID.

4. When vapour of nitrobenzene mixed with hydrogen is passed over heated platinum sponge, there is obtained amongst other products a yellowish oil, forming with hypochlorite of calcium a blue substance which is reddened by acids and turned blue again by alkalis. It is insoluble in water, soluble in alcohol and ether, and is neutral to litmus. (G. Jumel, Bull. Soc. Chim. 1861, p. 47.)

5. Nitrobenzene heated with sulphide of carbon to 160° is converted into aniline. (Schlagdenhauffen, J. Pharm. [3] xxxiv. 175.)

For other modes of effecting this transformation, see ANILINE under PHENYLAMINES.

6. Nitrobenzene treated with 2 pts. iron filings and ½ pt. strong hydrochloric acid is converted into a red colouring matter called erythrobenzin. After 24 hours' contact the solid mass is to be triturated and exhausted with water, the clear solution precipitated with common salt, and the product purified by resolution and precipitation. (F. Laurent and J. Castlehaz, Rep. Patent Inventions, Oct. 1862, p. 339.)

7. Dinitrobenzene treated with *iron-filings* and *acetic acid*, is converted into phenylene-diamine, $C^6H^4(NO^2)^2 + H^{12} = 4H^2O + N^2.H^4(C^6H^4)''$. (A. W. Hofmann, Proc. Roy. Soc. xi. 518.)

**NITROBENZOENE.** Syn. with Hydride of Nitrobenzoyl (see BENZYL, HYDRIDE OF, i. 574).

**NITROBENZOIC ACIDS.** See BENZOIC ACID (i. 455).

**NITROBENZONITRILE.** See BENZONITRILE (i. 564). For the action of sulphide of ammonium on this compound, see SULPHAMIDOBENZAMINE.

**NITROBENZOYL, PEROXIDE OF.** See PEROXIDES.

**NITROBENZONE** or **NITROBENZOPHENONE.** See BENZONE (i. 562).

**NITROBENZOYL-BENZOIN.** See BENZOIN (i. 560).

**NITROBROMO-PHENIC** or **-CARBOLIC ACID.** See PHENOL, DERIVATIVES OF.

**NITROBUTYRONIC ACID.** Syn. with BUTYRO-NITRIC ACID (i. 698).

**NITROCALCITE.** Native nitrate of calcium (see NITRATES).

**NITROCAPRIC ACID.** $C^{10}H^{19}(NO^2)O$.—Produced, together with nitrocaprylic acid, by the action of boiling nitric acid on the non-volatile fatty acids of cocoa-nut oil. (Wirz, Ann. Ch. Pharm. civ. 289.)

**NITROCAPRYLIC ACID.** See CAPRYLIC ACID (i. 745).

**NITROCARBOLIC ACID.** Syn. with NITROPHENIC ACID.

**NITROCELLULOSE.** See CELLULOSE (i. 819) and PYROXYLIN.

**NITROCHLOROBENZENE.** See CHLORIDE OF DINITROPHENYL, under PHENYL, CHLORIDE OF.

**NITROCHLOROBENZOIC ACIDS.** These acids are produced by the action of fuming nitric acid on the corresponding chlorobenzoic acids. *Nitromonochlorobenzoic acid*, $C^7H^4Cl(NO^2)O^2$, is slightly soluble in cold, easily in hot water, and crystallises in needles which melt at 205(?) Its silver-salt is a white precipitate which separates from water in flat crystals. *Nitrodichlorobenzoic acid*, $C^7H^2Cl^2(NO^2)O^2$, is a yellowish oil which does not solidify even after long standing. (Otto, Ann. Ch. Pharm. cxxii. 129.)

**NITROCHLORONICEIC ACID.** } See Chloronicic Acid (i. 920).
**NITROCHLORONICENE.** }

**NITROCHOLIC ACID.** $CH^2N^4O^5$? (Redtenbacher, Ann. Ch. Pharm. lvii. 145.)—An acid produced by the action of nitric acid on choloïdic acid (i. 929). The heavy oil which condenses in the receiver has an acid reaction, but is not a uniform substance. When washed with water and left in contact with aqueous potash, it acquires a yellow colour, and if the alkaline solution is concentrated, deposits lemon-yellow crystals of nitrocholate of potassium. To obtain the whole of this salt, the alkaline solution is decanted from the unaltered oil and evaporated in a vacuum. It may be purified by redissolving the crystals in tepid water, and again evaporating in a vacuum.

*Nitrocholate of potassium*, $CHKN^4O^5$?, has a lemon-yellow colour, and apparently the same form as ferrocyanide of potassium; it has a slightly intoxicating odour, and is not permanent in the air. The crystals, as they dry even in vacuo, and especially if heated, split into a great number of small fragments, acquiring at the same time a powerful odour and apparently suffering decomposition. The solution of the salt decomposes under the same circumstances. When boiled for a long time, it yields crystals of saltpetre. When decomposed by an acid, dilute sulphuric acid for example, it yields nitrous acid, nitric acid, a fat oil and hydrocyanic acid, products which may likewise be obtained from the mother-liquor of the crude nitrocholate. Nitrocholate of potassium does not precipitate metallic salts.

**NITROCHRYSENE.** See Chrysene (i. 958).

**NITROCINNAMENE.** See Cinnamene (i. 983).

**NITROCINNAMIC ACID.** See Cinnamic Acid (i. 983).

**NITROCINNAMIDE.** See Cinnamide (i. 989).

**NITROCINNANISIDIDE.** *Nitranisyl-cinnamide* or *Cinnitraniside*, $C^{14}H^{14}N^2O^4$ (see i. 304, 989).

**NITROCOCCUSIC ACID.** A product of the action of nitric acid on carmine (i. 804).

**NITROCODEINE.** See Codeine (i. 1068).

**NITROCOUMARIN.** See Coumarin (ii. 94).

**NITROCUMENE** or **NITROCUMOL.** See Cumene (ii. 174).

**NITROCRESYLIC ACID.** See Cresylic Alcohol (ii. 207).

**NITROCUMENYLAMINE** or **NITROCUMIDINE.** See Cumenylamine (ii. 178).

**NITROCUMINIC ACID.** See Cuminic Acid (i. 178).

**NITROCYMENE** or **NITROCYMOL.** See Cymene (ii. 296).

**NITRODRACONESIC ACID.** Syn. with Nitranisic Acid.

**NITRODICHLOROPHENIC ACID.** *Nitrodichlorophenol*, *Nitrodichlorocarbolic acid.* (See Phenol, Derivatives of.)

**NITRODRACYLAMIDE.** $C^7H^6N^2O^3$. Isomeric with nitrobenzamide (i. 541). Obtained by the action of ammonia on nitrodracylic ether. (Wilbrand and Beilstein.)

**NITRODRACYLIC ACID.** *Paranitrobenzoic acid.* $C^7H^4(NO^2)O^2$. (Wilbrand and Beilstein, Ann. Ch. Pharm. cxxvi. 255; cxxviii. 257.—G. Fischer, *ibid.* cxxvii. 137; cxxx. 128.)—An acid isomeric with nitrobenzoic acid, produced by the action of fuming nitric acid on toluene (hydride of benzyl). It was first observed by Glenard and Boudault (Ann. Ch. Pharm. xlviii. 344), who however assigned to it the formula $C^{14}H^5(NO^4)O^4$. Fischer obtained it as a secondary product in preparing nitrobenzene from benzene containing toluene. By agitating the crude nitrobenzene thus obtained with dilute soda-ley, and neutralising the alkaline solution with hydrochloric acid, the acid separated in flocks, which were purified by recrystallisation with

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addition of animal charcoal. Wilbrand and Beilstein saturate fuming nitric acid with toluene, keeping the liquid cool; boil the mixture for four or five days with excess of nitric acid; dilute the liquid with water; distil off the greater part of the nitric acid and the unattacked toluene; agitate the residue with dilute ammonia; supersaturate with nitric acid; and purify the separated nitrodracylic acid by repeated solution in ammonia, precipitation with acid, and recrystallisation from alcohol. The mother-liquor retains a more soluble acid, not yet examined.

Nitrodracylic acid crystallises from solution in yellowish laminæ, and sublimes in slender needles. It is easily soluble in alcohol, ether, and boiling water; melts at 240° (nitrobenzoic acid at 127°).

*Nitrodracylate of Ammonium*, $C^7H^4(NH^4)(NO^2)O^2.2H^2O$, crystallises in faint rose-coloured very efflorescent laminæ (Wilbrand and Beilstein). On saturating an ammoniacal solution with sulphydric acid, and adding acetic acid to the filtrate, a crystalline precipitate is formed consisting of oxydracylamic acid, $C^7H^7NO^3$ or $\left.\begin{matrix}(C^7H^4O)''\\ H^3\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix}$, isomeric with oxybenzamic acid (Fischer). The same acid is produced by treating nitrodracylic acid with tin and hydrochloric acid (W. and B.). See OXYDRACYLAMIC ACID.

*Nitrodracylate of Barium*, $2C^7H^4Ba(NO^2)O^2.5H^2O$ or $C^{14}H^8\mathit{Ba}''(NO^2)^2O^4.5H^2O$, crystallises in transparent yellow prisms (W. and B.); the *calcium-salt* in colourless needles containing $C^7H^4Ca(NO^2)O^2.4H^2O$ or $C^{14}H^8\mathit{Ca}''(NO^2)^2O^4.8H^2O$ (W. and B.); in splendid large tables, $C^{14}H^8\mathit{Ca}''(NO^2)^2O^4.9H^2O$, which give off 8 at. water over oil of vitriol, and the remainder at 150° (Fischer). [Nitrobenzoate of calcium crystallises, according to Fischer, in indistinct nodules with 2 at. water, which it gives off between 130° and 190°.]

The *lead-salt*, $C^{14}H^8\mathit{Pb}''(NO^2)^2O^4$, crystallises in needles (W. and B.; Fischer); the *magnesium-salt* in thick rhombohedral crystals (W. and B.); the *silver-salt* in needles (Fischer; W. and B.); the *sodium-salt* in large yellow prisms. (W. and B.)

**NITRODRACYLIC ETHERS.** The *ethylic ether*, $C^7H^4(C^2H^5)(NO^2)O^2$, obtained by treating the alcoholic solution of the acid with hydrochloric acid gas, crystallises from alcohol in large inodorous laminæ, melting at 57°.—The *methylic ether*, $C^7H^4(CH^3)(NO^2)O^2$, forms nacreous laminæ melting at 96°. (Wilbrand and Beilstein, *loc. cit.*)

**NITROERYTHROMANNITE.** *Nitroerythrin.* See ERYTHROMANNITE (ii. 505).

**NITROETHYLIC ACID (DI-).** $C^2H^6N^2O^2$. (Frankland, Phil. Trans. 1857, p. 59; Chem. Soc. J. xi. 89.)—This acid is obtained as a zinc-salt, $C^2H^5ZnN^2O^2$ or rather $C^4H^{10}\mathit{Zn}''N^4O^4$, by the combination of 4 at. nitric oxide (NO) with 1 at. zinc ethyl ($C^4H^{10}\mathit{Zn}''$). When zinc-ethyl, either pure or dissolved in ether, is passed up by small quantities into dry nitric oxide confined over mercury, the gas is absorbed slowly, but completely and in large quantity, without the production of any other gas. The solution may be accelerated by agitation. At the end of one to four days, rhomboïdal crystals of a zinc-salt begin to be deposited, and increase in number till the liquid finally solidifies.

[For a description of the mode of preparing it in larger quantities, see the memoir above cited; also *Gmelin's Handbook*, xii. 555.]

The salt obtained as above is a compound of dinitroethylate of zinc with zinc-ethyl, $C^4H^{10}\mathit{Zn}''N^4O^4.\mathit{Zn}''(C^2H^5)^2$. It dissolves in anhydrous ether, and separates from the solution in large, colourless, transparent, rhomboïdal crystals, which instantly become opaque on exposure to the air, owing to the formation of an oxidised product. Heated to between 180° and 190° it gives off a mixture of carbonic anhydride, ethylene, hydride of ethyl, nitrogen, and nitrous oxide.

A *basic dinitroethylate* or *oxy-dinitroethylate of zinc*, $C^4H^{10}\overset{''}{\mathit{Zn}}N^4O^4.\overset{''}{\mathit{Zn}}O$, is obtained by treating the preceding salt with water, which decomposes the zinc-ethyl, with evolution of hydride of ethyl and formation of oxide of zinc. The oxy-dinitroethylate remains dissolved in the water, and on passing carbonic anhydride through the solution, carbonate of zinc is precipitated, and a solution is obtained which when evaporated to dryness, yields *neutral dinitroethylate of zinc*, as a radiated crystalline mass composed of $C^4H^{10}\mathit{Zn}''N^4O^4.H^2O$; and this when heated to 100°, yields the anhydrous salt, which takes fire at about 300°, burning with a beautiful bluish-green flame.

*Dinitroethylic acid* is obtained in dilute aqueous solution by decomposing a dilute solution of the zinc-salt with sulphuric acid and distilling in a vacuum, or by decomposing the barium-salt with just sufficient sulphuric acid to precipitate the base. It has a pungent odour, reddens litmus strongly, and is very unstable, decomposing gradually even at ordinary temperatures, and rapidly when slightly heated, with evolution of gases and white vapours.

The dinitroethylates are all soluble in water and in alcohol, and most of them crystallise with more or less difficulty. They are all violently acted on by strong nitric acid, the dinitroethylic acid being decomposed and a nitrate of the base produced. Dilute nitric acid acts in a similar way, but more slowly. They all melt at a little above 100°. The potassium-, sodium-, calcium-, and barium-salts deflagrate explosively like loose gunpowder, at a temperature considerably below redness.

*Dinitroethylate of Barium*, $C^4H^{10}Bba''N^4O^4$, prepared by treating the zinc-salt with excess of caustic baryta, removing the excess of baryta by carbonic acid, &c., is neutral, uncrystallisable, very deliquescent, and very soluble in water.—The *calcium-salt*, $C^4H^{10}Cca''N^4O^4.3H^2O$, prepared like the barium-salt, crystallises in silky needles which give off 2 at. water at 100°. By distillation with ethyl-sulphate of potassium it appears to yield dinitroethylate of ethyl.—The *copper-salt*, $2C^4H^{10}Ccu''N^4O^4.H^2O$, prepared from the barium-salt by double decomposition, forms a solution of a splendid purple colour, which, by evaporation in a vacuum, yields purple four-sided needles several inches long.—The *magnesium-salt*, $C^4H^{10}Mmg''N^4O^4$, prepared by decomposing the zinc-salt with magnesia, separates from the solution, when concentrated over a water-bath, in granular crystals which melt at 100°, and dry up to a solid amorphous mass consisting of the anhydrous salt.—The *silver-salt*, $C^2H^5AgN^2O^2$, prepared like the copper-salt, is very soluble in water, and crystallises in very light scales, which are rapidly decomposed on exposure to light. A compound of this salt with nitrate of silver, $C^2H^5AgN^2O^2.AgNO^3$, is obtained as a crystallo-granular, sparingly soluble precipitate, on mixing concentrated solution of dinitroethylate of zinc, and nitrate of silver.

**NITROEUXANTHIC ACID.** See EUXANTHIC ACID (ii. 610).

**NITROFERRICYANIDES.** *Nitroprussides.* (See CYANIDES OF IRON, ii. 250.)

**NITROFORM.** See NITROMETHIDES.

**NITROFRANGULIC ACID.** See FRANGULIN (ii. 707).

**NITROGEN.** *Azote. Gas azote. Stickluft. Stickstoff.* Atomic Weight, 14. Symbol, N.—This element was discovered by Rutherford in 1772. Lavoisier subsequently ascertained that atmospheric air is composed of oxygen and nitrogen gases, the latter of which he called *azote*, from its incapability of supporting life (α and ζωὴ). Chaptal afterwards gave it the name *nitrogen*, from its entering into the composition of nitre, nitric acid, &c.

Nitrogen constitutes about one-fifth of the volume of the atmosphere. It occurs also in the free state in the air-bladders of fish, and in other cavities of the bodies of animals and vegetables. In combination it occurs in native nitrates and ammoniacal salts, and in a vast number of organic compounds, especially those belonging to the animal kingdom.

*Preparation.* 1. *From the Air.*—Nitrogen may be separated from the air by burning in it any substance which forms with the oxygen a product that can easily be removed. Thus when phosphorus burns under a bell-jar standing over water in the pneumatic trough, phosphoric acid is produced, and is quickly absorbed by the water, which then rises into the jar till it fills about one-fifth of the space originally occupied by the air. The remaining gas, after being well shaken several times with fresh portions of water to remove the last traces of phosphoric acid, consists of nitrogen contaminated only with aqueous vapour and a trace of carbonic anhydride. When the gas is required quite pure, a better method of obtaining it is to pass air previously freed from carbonic anhydride by caustic potash and from aqueous vapour by oil of vitriol, over ignited metallic copper; the oxygen then enters into combination with the copper and the nitrogen, may be received in a vessel exhausted of air. Or air from a gas-holder may be passed through a large bottle filled with a mixture of moistened sawdust and precipitated oxide of iron which has been converted into sulphate of iron by a current of sulphydric acid gas. After its transit through this vessel, the air, deprived almost entirely of its oxygen, should be passed through a series of four U-tubes, the first two containing solution of pyrogallate of potassium a caustic potash to absorb the carbonic anhydride and residual oxygen, the last two containing oil of vitriol to absorb the aqueous vapour. This is a very convenient method in practice, as the sulphide of iron may be restored to efficient activity an indefinite number of times by passing sulphydric acid gas through the containing vessel.

2. *From Ammonia and its salts.*—*a.* By passing chlorine through aqueous ammonia:

$$4NH^3 + Cl^3 = N + 3NH^4Cl.$$

The liberated nitrogen may be freed from adhering ammonia by washing with sulphuric acid. Care must be taken to keep the ammonia in considerable excess, as otherwise the dangerous compound, chloride of nitrogen, may be formed by the action of the chlorine on the sal-ammoniac. According to Anderson (Chem. News, v. 246), the nitrogen obtained by this method is always mixed with oxygen.

β. Solution of nitrite of ammonium when boiled splits up into water and nitrogen, $NH^4NO^2 = 2H^2O + N^2$. But as this salt is difficult to prepare, it is better to substitute for it a mixture of sal-ammoniac and nitrite of potassium:

$$NH^4Cl + KNO^2 = KCl + 2H^2O + N.$$

This is the easiest of all methods of obtaining pure nitrogen. The solution of nitrite of potassium may be prepared by passing nitrous anhydride, evolved from starch and nitric acid, into solution of potash of specific gravity 1·38, till it acquires a decided acid reaction, when it is to be neutralised by further addition of the alkali. This solution undergoes no change by keeping, and when required to yield nitrogen, must be mixed with three times its volume of a concentrated solution of sal-ammoniac.

γ. Nitrate of ammonium heated in the dry state with sal-ammoniac also yields nitrogen, together with chlorine, which may be absorbed by slaked lime or caustic potash:

$$2(NH^4)NO^3 + NH^4Cl = N^3 + Cl + 6H^2O.$$

Nitrogen may also be obtained from nitrate of ammonium by dipping a piece of metallic zinc into the fused salt.

δ. Or it may be procured by saturating oil of vitriol with nitric oxide gas, adding sulphate of ammonium, and heating to 130°.

3. From *Animal substances.*—Muscle and other animal substances gently heated with dilute nitric acid give off nitrogen, together with a little nitric oxide, which may be removed by passing the evolved gas through a solution of ferrous sulphate.

*Properties.*—Nitrogen is a colourless uncondensable gas, of specific gravity 0·972; tasteless, inodorous, and without action on vegetable colours. It is sparingly soluble in *water*, 100 measures of which at 15° dissolve only 1½ measures of nitrogen. (See GASES, ABSORPTION OF, ii. 795.) It is incombustible, and does not support the combustion of ordinary combustibles (sulphur, phosphorus, carbon, hydrocarbons, &c.). It may be breathed for a short time, but does not support respiration. It is not poisonous, but an animal immersed in it dies, simply for want of oxygen. Its function in the atmosphere, as regards combustion and respiration, appears to be merely that of a diluent, preventing the too rapid action that would take place in an atmosphere of unmixed oxygen.

In the free state, nitrogen exhibits for the most part but little chemical activity. The metals *titanium*, *tantalum*, *tungsten*, and probably a few others, combine with it however, and even burn in it, and under certain circumstances it may be made to unite directly with *hydrogen*, *oxygen*, and *carbon*. Thus when a long series of electric sparks is passed through a mixture of oxygen and nitrogen gases standing over a solution of caustic alkali, combination slowly takes place, and a nitrate of the alkali-metal is produced. Traces of nitric acid and nitrate of ammonium also result from burning hydrogen gas mixed with nitrogen in an atmosphere of air or oxygen. Nitrogen and hydrogen can also unite, when one or both the gases are in the nascent state, to form ammonia (i. 182). The direct union of carbon with nitrogen to form cyanogen, takes place when nitrogen gas or atmospheric air is passed over an ignited mixture of charcoal and potash or baryta. (See CYANIDES, ii. 198, 239.)

The slight affinity existing between nitrogen and other elements gives a peculiar character to its compounds, many of which are extremely prone to decomposition, *e.g.* the azotised principles of the animal and vegetable organism. Many nitrogen-compounds also, especially those which contain the oxygenated radicle *nitryl*, $NO^2$, are highly explosive.

Nitrogen belongs to the pentad group of elements (iii. 967), including also phosphorus, arsenic, antimony and bismuth. It enters however into combination with other elements in several proportions; thus there is a complete series of oxides of nitrogen, in which the ratio of the number of nitrogen atoms to that of the oxygen-atoms ranges between the limits 2 : 1 and 2 : 5; and Griess has shown that in a variety of organic bodies, a single atom of nitrogen may be substituted for 1 or for 3 atoms of hydrogen. In ammonia and its numerous substitution derivatives, a single atom of nitrogen is united with 3 atoms of hydrogen or of radicles equivalent thereto; in the ammonium-salts and their analogues, on the other hand, an atom of nitrogen is united with 5 atoms of hydrogen and other monatomic elements, or with equivalent quantities of polyatomic

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elements: *e.g.* chloride of ammonium, $N\left\{\begin{matrix}H^4\\Cl\end{matrix}\right.$; sulphate of ammonium, $N^2\left\{\begin{matrix}H^8\\(SO^4)''\end{matrix}\right.$; orthophosphate of ammonium, $N^3\left\{\begin{matrix}H^{12}\\(PO^4)'''\end{matrix}\right.$.

**NITROGEN, BORIDE OF.** See Boron, Nitride of (i. 635).

**NITROGEN, BROMIDE OF.** $NBr^3$?—Formed by decomposing chloride of nitrogen with aqueous bromide of potassium. Dense blackish-red, very volatile oil, having an odour like that of the chloride, and exploding violently by contact with phosphorus and arsenic. (Millon, Ann. Ch. Phys. lxix. 75.)

**NITROGEN, CHLORIDE OF.** $NCl^3$?—This highly explosive compound was discovered by Dulong in 1812. It may be prepared: 1. By filling a bottle carefully cleaned and freed from every trace of greasy impurity, with chlorine gas, and inverting it over a leaden dish containing a weak solution of some ammoniacal salt, a solution of 1 pt. sal-ammoniac in 12 to 15 pts. water being generally employed. The chlorine is then gradually absorbed, while yellow oily drops of chloride of nitrogen form on the surface of the liquid, and soon fall to the bottom. The reaction is—

$$NH^4Cl + Cl^6 = 4HCl + NCl^3.$$

2. When a small lump of sal-ammoniac is suspended in an aqueous solution of hypochlorous acid, the same compound is deposited, being produced according to the reaction:

$$NH^4Cl + 3HClO = HCl + 3H^2O + NCl^3.$$

This is a better mode of preparation than the former.

Chloride of nitrogen is a thin yellow oil of specific gravity 1·653. It volatilises quickly in the air, giving off a peculiar penetrating odour, and attacking the eyes strongly. When heated to nearly 100°, or when treated with any oil or fat, or with turpentine, phosphorus, and many other substances, it decomposes with an extremely violent though local explosion. A single drop of it exploded on a glass or porcelain dish, shatters the vessel to atoms. By hydrochloric, sulphydric, or sulphurous acid, it is decomposed without explosion, and these reactions afford the means of analysing the compound. The results of different chemists who have examined it do not, however, agree. Acording to Bineau (Ann. Ch. Phys. [3] xv. 71) it has the formula $NCl^3$; according to Millon (Ann. Ch. Phys. [2] lxix. 75), it is $N^3H^6Cl^3 = NCl^3.2NH^3$; according to Gladstone (Chem. Soc. Qu. J. vii. 51), $N^2HCl^3 = NCl^3.NHCl^3$. The reaction with sulphurous acid is, according to Bineau's formula,

$$NCl^3 + 3H^2SO^3 + 3H^2O = NH^4.H.SO^4 + 2H^2SO^4 + 3HCl;$$

according to Gladstone's,

$$N^2HCl^3 + 5H^2SO^3 + 5H^2O = 2(NH^4.H.SO^4) + 3H^2SO^4 + 5HCl.$$

**NITROGEN, CHLOROPHOSPHIDE OF.** $NPCl^2$. See Phosphorus, Chloronitride of.

**NITROGEN, CHLOROSULPHIDE OF.** $NS^2Cl$ or $N^2S^3.SCl^2$.—When the compound $2NH^3.SCl^2$ (obtained by bringing ammonia-gas slowly in contact with protosulphide of chlorine) is heated for some hours to 100° in a glass tube, it is converted into a yellow mixture of sal-ammoniac and chlorosulphide of nitrogen:

$$2(2NH^3.SCl^2) = 3NH^4Cl + NS^2Cl.$$

On heating this mixture, sal-ammoniac is given off, and the chlorosulphide of nitrogen is resolved into nitrogen, sulphur and disulphide of chlorine—

$$2NS^2Cl = N^2 + S^2Cl^2 + S^2.$$

The same mixture dissolves completely in water, and the solution, which is yellow at first, becomes turbid after a while and slowly deposits a brown powder, and is then found to contain sal-ammoniac and hyposulphurous acid, with a trace of sulphydric acid. The principal reaction may be expressed by the equation:

$$NS^2Cl + 3H^2O = NH^4Cl + H^2S^2O^3.$$

The brown powder appears to be composed of 7 at. sulphur, 3 at. hydrogen and 3 at. nitrogen, with a trace of chlorine.

When carbonic anhydride is passed through a hot solution of sulphide of nitrogen in protosulphide of chlorine, a small quantity of chlorosulphide of nitrogen sublimes after a while in yellow crystals. The compound thus prepared gives a blue colour with ammonia. (Soubeiran, Ann. Ch. Phys. lxvii. 87, 101. See also *Gmelin's Handbook*, ii. 475.)

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**NITROGEN, DETECTION AND ESTIMATION OF.** *Reactions.*—The properties of nitrogen in the free state have been already described. They are essentially negative. A gas which does not burn in the air or support the combustion of a taper, which has neither an acid nor an alkaline reaction, does not render lime-water turbid, and is not absorbed by caustic alkalis or by acids, may be pronounced to be nitrogen. In like manner, in examining a gaseous mixture, after all the absorbable gases have been removed by appropriate reagents, hydrogen and hydrocarbons by explosion with oxygen, and oxygen itself by explosion with hydrogen, the residual gas can consist of nothing but nitrogen, and its volume may be determined by direct measurement. (See ANALYSIS (VOLUMETRIC) OF GASES, i. 273, 280, 285; also ATMOSPHERE, i. 535.)

The methods of detecting and estimating nitrogen in liquid and solid compounds in which it is associated with carbon and hydrogen, viz. in organic bodies, have been already fully described in the article ANALYSIS, ORGANIC (i. 225, 239). The method of calcination with soda-lime may also be applied to the determination of nitrogen in many inorganic compounds, *e.g.* the nitride of boron (i. 635), and certain metallic nitrides.

Nitride of boron may also be analysed by mixing it with a known weight of pure oxide of lead, drenching the mixture with nitric acid, evaporating it to dryness, and calcining it in a platinum crucible. The excess of weight of the residue over the original weight of the lead-oxide gives the quantity of boric anhydride produced by the oxidation of the boron, whence the amount of boron in the compound may be calculated, and the nitrogen determined by difference.

Nitride of phosphorus may be analysed in a similar manner; or by heating it to redness in a stream of hydrogen, whereby the nitrogen is converted into ammonia, which may be condensed in hydrochloric acid, and estimated as platinum-salt.

Sulphide of nitrogen is analysed by oxidising the sulphur with nitric acid, or with hydrochloric acid and chlorate of potassium; or by dissolving the compound in dilute potash, and oxidising with hypochlorite of potassium. The sulphuric acid thus formed is precipitated by a barium-salt, the quantity of sulphur thence calculated, and the nitrogen determined by difference.

The compounds of nitrogen with chlorine, bromine, and iodine, may be analysed by decomposing them with hydrochloric, sulphydric or sulphurous acid, and determining the quantities of ammonia, and of hydrochloric acid, &c., thereby produced (see iii. 281, and iv. 64).

The nitrogen in metallic nitrides may, in most cases, be accurately determined by igniting the compound, reduced to very fine powder, with *oxide of copper* in a combustion-tube. The metal is thereby oxidised, and the nitrogen is given off as gas, which may be collected and measured. It does not appear that any oxides of nitrogen are formed during the combustion. If the compound also contains hydrogen, that element will be converted into water, which may be condensed in a chloride of calcium tube, as in organic analysis. In some cases exact results may be obtained by igniting the nitride in a current of *air* or *oxygen*—whereby the metal is oxidised, while the nitrogen escapes—weighing the resulting oxide, thence determining the amount of metal, and the nitrogen by difference.

Another method of decomposing metallic nitrides is to ignite them in a state of extremely fine division in a stream of *hydrogen gas*. The nitrogen is then converted into ammonia, which may be condensed in hydrochloric acid, while the metal remains in the free state. If an oxide is likewise present, water will be formed; and if it be condensed by chloride of calcium or hydrate of potassium and weighed, its weight will give by calculation the quantity of oxide present in the metallic compound. There are a few metallic nitrides which are not decomposed by hydrogen; such is the case with nitride of chromium.

The method very frequently adopted for analysing metallic nitrides is to fuse them in the state of fine powder with *hydrate of potassium* or *soda-lime*, whereby the nitrogen is converted into ammonia. Some nitrides, however, are not completely decomposed by this treatment, and nitride of chromium resists it altogether. Whether the decomposition of these nitrides would be assisted by addition of sugar, as in the analysis of certain organic nitrogen-compounds (i. 246), is a point which does not appear to have been ascertained by experiment.

The quantity of metal in the more refractory metallic nitrides may be determined by fusing the compound with a mixture of *alkaline carbonate* and *nitrate*, whereby the nitrate is oxidised. These compounds may also be oxidised by digestion in a strong solution of an *alkaline hypochlorite*, the nitrogen being at the same time given off as gas.

Lastly, these more refractory nitrides may be analysed by fusion with *acid sulphate of potassium*. This method has been applied by Wöhler to the analysis of the crystals of nitrocyanide of titanium found in iron smelting furnaces (ii. 273). The crystals, reduced to fine powder, were dissolved by fusion in the previously melted salt

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contained in a small retort; the evolved gases, consisting of nitrogen, carbonic anhydride (from the cyanogen) and sulphurous anhydride, were passed through a tube containing lumps of potash, to absorb the last two gases; and the nitrogen was collected and measured (see **Rose's** *Chimie Analytique*, ii. 1081).

It is often of importance to detect and estimate the presence of very small quantities of nitrogen in metals, inasmuch as the peculiar properties of certain metals prepared by particular processes, are sometimes attributed to the presence of these minute quantities of nitrogen. Thus the difference in quality of various kinds of steel has been partly attributed, by **Frémy** and others, to the greater or smaller quantities of nitrogen contained in them. On the other hand, a series of experiments recently made by Messrs. **Stuart** and **Baker** (Chem. Soc. J. xvii. 390), in which different kinds of steel in a state of very minute division were ignited in hydrogen gas, have shown that when proper precautions were taken to prevent access of nitrogen from the air or other extraneous sources, the quantity of ammonia formed is almost imperceptible; hence they consider it probable that the small quantities of nitrogen found in steel by other observers may have been due to errors of experiment, and at all events that the existence of nitrogen in steel cannot be regarded as proved. **Frémy**, however, does not consider the method of ignition in hydrogen as well adapted for the precise determination of the quantity of nitrogen contained in steel, but is of opinion that the only method capable of yielding trustworthy results is the direct oxidation of the steel by combustion, as in organic analysis, and the determination of the nitrogen by measurement. (**Pelouze** et **Frémy**, *Traité*, 3me. Ed. iii. 412.)

The **oxides of nitrogen** are analysed either by exploding them with hydrogen (i. 285), or by passing them over red-hot copper, which removes the oxygen and leaves the nitrogen. When carbon and hydrogen are likewise present, as in organic compounds, the substance must be burnt with oxide of copper, and the evolved gases passed over red-hot metallic copper (l. 242).

The methods especially adapted for the analysis of **nitrates** and **nitrites** will be described further on (pp. 71, 84).

*Atomic Weight of Nitrogen.*—The weights of equal volumes of hydrogen and nitrogen at the same pressure and temperature are, according to Regnault's experiments, as 1 : 14·06; hence, on the assumption that equal volumes of elementary gases contain equal numbers of atoms, the atomic weight of nitrogen should be 14·06.

**Svanberg** (Berz. Jahresb. xxii. 39), by the analysis of nitrate of lead, obtained for nitrogen the number 13·95; **Penny** (Phil. Trans. cxxix. 13), from the analysis of nitrate of sodium, found N = 14·02.

The experiments of **Pelonze** (Compt. rend. xx. 1047) and **Marignac** (Ann. Ch. Pharm. lix. 289), on the quantity of chloride of ammonium required to precipitate 1 pt. of silver from its solution in nitric acid, give—if Ag = 108, and Cl = 35·5—as a mean result, N = 13·99; and if Ag = 107·98, Cl = 35·46, then N = 14·01.—Marignac has further determined the weight of nitrate of silver produced by treating a known weight of metallic silver with nitric acid. 100 pts. silver gave, as a mean of five experiments, 157·2 pts. nitrate: hence (for Ag = 108) N = 14. **Stas** (Ann. Ch. Pharm. Suppl. i. 62) by the same method found N = 14·041.—Lastly, **Marignac** finds that 100 pts. chloride of potassium require for complete decomposition, on the average, 227·9 pts. nitrate of silver (max. 228·09; min. = 227·81), whence if Ag = 107·98, Cl = 35·46 and K = 39·11, we find N = 14·03.

These several results differ about equally in excess and defect from the whole number 14, which is accordingly received as the true atomic weight of nitrogen.

**NITROGEN, IODIDE OF.** See Iodamides (iii. 280).

**NITROGEN, OXIDES AND OXYGEN-ACIDS OF.** Nitrogen forms a very complete series of oxides, as represented in the following table:

| | |
|---|---|
| Protoxide or Nitrous oxide | $N^2O$ |
| Dioxide or Nitric oxide | $N^2O^2$ or $NO$ |
| Trioxide or Nitrous anhydride | $N^2O^3$ |
| Tetroxide or Nitric peroxide | $N^2O^4$ or $NO^2$ |
| Pentoxide or Nitric anhydride | $N^2O^5$. |

All these compounds may be produced directly or indirectly from nitric acid and reconverted into it. The three higher oxides are decomposed by water, yielding the corresponding acids; thus:

$$N^2O^3 + H^2O = \underset{\text{Nitrous acid.}}{2HNO^2}$$

$$N^2O^4 + H^2O = \underset{\text{Nitrous acid.}}{HNO^2} + \underset{\text{Nitric acid.}}{HNO^3}$$

$$N^2O^5 + H^2O = \underset{\text{Nitric acid.}}{2HNO^3}$$

### PROTOXIDE OF NITROGEN or NITROUS OXIDE. $N^2O$.

This compound, which is gaseous at ordinary temperatures, was discovered by Priestley in 1776, and minutely examined by Davy in 1800, who first noticed the lively stimulating effects produced by its inhalation, whence its popular name of *Laughing gas.*

*Formation and Preparation.*—1. By gently heating nitrate of ammonium in a flask or retort to a temperature not exceeding 250°. The salt puts on the appearance of ebullition, and is entirely resolved into water and nitrous oxide:

$$(NH^4)NO^3 \;=\; N^2O \;+\; 2H^2O.$$

The gas may be collected over brine, warm water, or mercury. If the temperature of the fused salt is allowed to rise too high, a more complex decomposition ensues, attended with the evolution of white fumes of nitrate and nitrite of ammonium, and of nitrogen, nitric oxide and ammoniacal gases. Moreover this decomposition is sometimes attended with explosion. If the gas is to be used for inhalation, great care must be taken to ensure that the nitrate of ammonium used is free from sal-ammoniac, otherwise the product will be contaminated with chlorine.

2. When granulated zinc is acted upon by nitric acid diluted with eight or ten times its volume of water, very pure nitrous oxide gas is slowly evolved:

$$10HNO^3 \;+\; Zn^8 \;=\; 8ZnNO^3 \;+\; 5H^2O \;+\; N^2O.$$

3. Nitrous oxide may also be obtained by decomposing nitric acid or a nitrate with a solution of stannous chloride in hydrochloric acid; by acting upon sal-ammoniac with nitric acid of specific gravity 1·2; by slowly passing nitric oxide gas through a solution of sulphurous acid or an acid sulphite; by decomposing nitrosulphate of ammonium; and by many other reactions; but when required in quantity, it is always prepared from nitrate of ammonium.

*Properties.*—Nitrous oxide is at ordinary temperatures a colourless, feebly refrangible gas, of specific gravity 1·495 $\left(= \dfrac{2\,.\,14 + 16}{2} \times 0{\cdot}0693\right)$. It has a faint agreeable odour and sweetish taste. When respired for four or five minutes, it produces a lively intoxication, often attended with a disposition to muscular exertion and violent laughter. Animals immersed in it become restless and die after some time. It is somewhat soluble in *water*, 100 pts. of which absorb 130 volumes of the gas at 0°, 78 vol. at 15°, and 61 vol. at 24°. (See GASES, ABSORPTION OF, ii. 796.) It also dissolves in *ether* and in the *fixed* and *volatile oils*. Neither the gas nor any of its solutions has any action upon vegetable colours.

Nitrous oxide may be reduced to the liquid and to the solid state. The liquid is obtained by heating perfectly dry nitrate of ammonium at the end of a bent glass tube hermetically sealed, till the whole has distilled over to the cold end; then this end is heated, and so on two or three times till the greater part of the salt is decomposed. In the cooler end, two strata of liquid condense, the lower of which is water containing nitrous acid and nitrous oxide in solution, the upper liquid nitrous oxide. The apparatus is very liable to burst with extreme violence, so that the greatest caution is required in using it (Faraday). The liquid compound may also be obtained by mechanical compression of the gas. (Natterer, Pogg. Ann. xii. 132.)

Liquid nitrous oxide is colourless and very mobile. Its specific gravity at 7°, and under a pressure of 50 atmospheres, was found to be 0·908. It boils at about −88°. A single drop of it placed upon the hand produces a wound like a burn. Metals dipped into it make a hissing noise, like that produced by quenching red-hot iron in water. Potassium, charcoal, sulphur, phosphorus, and iodine float on its surface without alteration. Ignited charcoal burns on its surface with a vivid light. It is miscible with ether and alcohol. Sulphuric and nitric acid are immediately frozen by it. Water also freezes, but at the same time causes the liquid nitrous oxide to evaporate with a degree of rapidity almost amounting to explosion. According to Faraday, nitrous oxide is the least refractive of all liquids.

By exposing liquid nitrous oxide to the cold produced by a bath of solid carbonic anhydride and ether (−100° C. or −150° F.), the compound is reduced to the solid state. Again, when liquid nitrous oxide is allowed to escape into the air, by opening the stopcock of the vessel in which it has been condensed, the first portion which escapes is reduced to the solid state. Solid nitrous oxide is a white snowy mass which, when placed upon the hand, melts, evaporates suddenly, and produces a blister like a burn. Mixed in vacuo with sulphide of carbon, it depresses the thermometer to −140° C. or −240° F. (Natterer.)

*Decompositions.*—1. Nitrous oxide gas is resolved into its elements by a series of electric sparks, or by transmission through a red-hot tube, 2 vol. of the gas yielding

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1 vol. oxygen and 2 vol. nitrogen. A coil of iron rendered incandescent by the electric current also decomposes it, with formation of ferric oxide, and liberation of a volume of nitrogen equal to that of the original gas. A similar effect is produced by the electric arc issuing from an iron point. An incandescent platinum coil produces a more complex decomposition, attended with formation of red vapours. (Buff and Hofmann, Chem. Soc. J. x. 279.)

2. Nitrous oxide forms explosive mixtures with many inflammable gases. When exploded with its own volume of *hydrogen*, it yields water and a volume of nitrogen equal to that of the original gas.

$$\underset{2\text{ vol.}}{N^2O} + \underset{2\text{ vol.}}{H^2} = H^2O + \underset{2\text{ vol.}}{N^2}$$

3. Nitrous oxide acts, like oxygen, as a supporter of combustion, but is distinguished from that gas by not forming red vapours when mixed with nitric oxide. A bright-glowing match introduced into nitrous oxide, bursts into flame and burns with a brilliancy almost equal to that which it exhibits in oxygen. Ignited *carbon* and its compounds inflame very readily in nitrous oxide gas; but other combustibles, *phosphorus* and *sulphur* for example, require to be very strongly heated in order to burn; the combustion, however, when once established, takes place with great brilliancy. *Sodium* heated in nitrous oxide takes fire and leaves a volume of nitrogen equal to that of the original gas. *Iron, zinc*, and other metals, in a state of ignition, also continue to burn in nitrous oxide.

### DIOXIDE OF NITROGEN OR NITRIC OXIDE, NO or $N^2O^2$.

Synonymes. *Binoxide of Nitrogen. Deutoxide of Nitrogen. Nitrosyl. Azotyl. Nitrous gas. Nitrous air. Salpetergas. Gas nitrosum.*—This gas, which was first investigated if not discovered by Priestley, may be prepared:

1. By acting on copper clippings or borings with nitric acid of specific gravity 1·2, made by diluting the strong acid with about twice its bulk of water. Nitrate of copper is then formed, and nitric oxide evolved:

$$4HNO^3 + Cu^2 = 3CuNO^3 + 2H^2O + NO.$$

The reaction, if it does not take place at once, may be set up by the application of a gentle heat; but the lower the temperature the purer is the resulting gas. When strong nitric acid is used, or the temperature rises high, the nitric acid is contaminated with free nitrogen. Other metals, lead, mercury, silver, and bismuth, for example, may be substituted for copper in the above reaction, but with them a strong acid or a higher temperature is required.

2. By decomposing nitrate of potassium or sodium with a solution of ferrous chloride in hydrochloric acid, or of ferrous sulphate in dilute sulphuric acid:

$$6Fe^2SO^4 + 5H^2SO^4 + 2KNO^3 = 3Fe^4(SO^4)^3 + 2HKSO^4 + 4H^2O + 2NO.$$

This process yields the gas abundantly and in a pure state.

3. Nitric oxide, more or less pure, is produced by many other reductions of nitrous or nitric acid; also by the oxidation of ammonia, as when that gas is passed over heated oxide of manganese.

*Properties and Reactions.*—Nitric oxide is a colourless uncondensable gas of specific gravity 1·0395 $\left(= \frac{14 + 16}{2} \times 0{\cdot}0693\right)$. It is very sparingly soluble in *water*. According to Henry, 1 vol. water at mean temperature absorbs $\frac{1}{20}$ of its volume of the gas. According to Bunsen, 100 vol. *alcohol* at 15° absorb 27·4 vol. of the gas.

Nitric oxide combines directly with free *oxygen*, producing deep orange-coloured fumes of variable composition, but consisting in great part of nitric peroxide. These red vapours dissolve in water, forming an acid solution, but nitric oxide itself is perfectly neutral to vegetable colours. From the characteristic nature of this reaction, nitric oxide may be advantageously employed to detect the presence of free oxygen in a gaseous mixture. It is necessary to observe, however, that *chlorine*, in presence of water, produces the same effect with nitric oxide, inasmuch as it decomposes the water and sets oxygen free. This reaction was in fact one of those which were formerly adduced in favour of the theory which regarded chlorine as a compound gas containing oxygen. Nitric oxide was formerly used, especially by Priestley and Cavendish, to estimate the proportion of oxygen in the air or other gaseous mixture, but the method is not capable of yielding exact results, on account of the difficulty of obtaining nitric oxide perfectly pure, and it has long since been superseded by more trustworthy methods. In consequence of the rapid conversion of nitric oxide into acid products when it comes in contact with the air, its actual taste, smell, and respirability have not been ascertained.

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Nitric oxide is absorbed freely by *nitric acid*, with probable conversion into nitric peroxide, and formation of a deep brown, green, or blue liquid, according to the concentration of the acid. It is likewise absorbed by *ferrous salts*, producing a deep brown, almost black coloration. The brown liquid thus formed contains 2 atoms of iron (at. w, = 56) to each molecule of nitric oxide, the formula of the compound being $2Ffe''SO^4.NO$. It gives up nearly the whole of the absorbed gas when heated, but becomes rapidly oxidised on exposure to the air. This compound is also formed when nitric or nitrous acid is added to the solution of a ferrous salt, and affords one of the most delicate tests for those acids (pp. 71, 82). Nitric oxide forms precisely similar compounds with *chromous salts;* it is likewise absorbed by *stannous* and *mercurous salts*, and forms crystalline compounds with *stannic chloride*, and with *sulphuric acid* or *anhydride.*

*Decompositions.*—1. Nitric oxide is a very stable compound, and if perfectly dry, is not decomposed by a red heat, or by ordinary electric sparks. Buff and Hofmann found, however, that it was slowly decomposed by the spark current of the induction coil. Moist nitric oxide is more easily decomposed by a succession of electric sparks into nitrogen and nitric acid.—2. By moist *iron filings*, *zinc filings*, *soluble sulphides*, *acid sulphites*, *stannous chloride*, and other reducing agents, it is slowly converted into nitrous oxide, frequently accompanied by ammonia.—3. Nitric oxide is completely converted into ammonia when mixed with excess of *sulphydric acid*, and transmitted over quicklime.—4. A mixture of *moist iron filings* and *sulphur* also reduces nitric oxide very completely, but chiefly to free nitrogen.—5. Ordinary combustibles do not burn in nitric oxide, but *phosphorus* and *carbon*, when introduced in full combustion, burn in the gas with great brilliancy.—6. With an equal volume of *hydrogen*, it forms a mixture which does not explode on the approach of a burning body, but burns quietly with a greenish flame.—7. Four volumes of nitric oxide passed over red-hot *charcoal* are converted into 2 vol. nitrogen and 2 vol. carbonic anhydride: $N^2O^2 + C = N^2 + CO^2$.—8. *Sulphur* does not burn in nitric oxide, but a mixture of the vapour of *sulphide of carbon* and nitric oxide gas inflames readily, producing a bright greenish flash of light.—9. Red-hot *iron* decomposes nitric oxide, with liberation of half its volume of nitrogen. With a coil of iron wire rendered incandescent by the electric current, the decomposition is easily and completely effected (Buff and Hofmann). *Potassium* and *sodium* effect similar decompositions when heated sufficiently to burn in the gas.

Nitric oxide enters into several compounds as a monatomic radicle (nitrosyl), replacing hydrogen atom for atom, as in the nitrites, the general formula of which is $\left.\begin{matrix}(NO)'\\M'\end{matrix}\right\}O$. It has for the most part a chlorous rather than a basylous character, nevertheless it is sometimes capable of replacing basylous hydrogen, as in chloride of nitrosyl, $NOCl$, and sulphate of nitrosyl, $H(NO)SO^4$. In nitrous ether, $C^2H^5(NO)O$, the nitrosyl may also be regarded as occupying the place of the basylous hydrogen-atom of alcohol, $C^2H^5.H.O$. According to Weltzien, nitric oxide is sometimes diequivalent or capable of displacing two atoms of hydrogen, a view which is in accordance with the fact that it forms a dichloride, $NOCl^2$, as well as a protochloride. (See NITROSYL.)

## NITROUS ANHYDRIDE, ACID, AND SALTS.

**Nitrous anhydride** or **Trioxide of nitrogen** = $N^2O^3$.—**Nitrous acid** = $H^2O.N^2O^3$ or $HNO^2$. Nitrous anhydride is formed, together with nitric peroxide, when nitric oxide comes in contact with oxygen in atmospheric air. It may be obtained pure by mixing 2 vol. nitric oxide with 1 vol. of oxygen in a vessel surrounded by a freezing mixture capable of producing an intense degree of cold. A blue liquid is then formed which emits red fumes, and is decomposed by water, yielding nitric acid and nitric oxide:

$$3N^2O^3 + 2H^2O = 2HNO^3 + 4NO + H^2O.$$

The same liquid is more easily obtained by heating 1 pt. of starch with 8 pts. of nitric acid of specific gravity 1·25, and passing the evolved gases, first through a drying tube two feet long containing fused chloride of calcium, and then into an empty tube cooled to −20° F. (−93·6° C.) by immersion in a mixture of pounded ice and crystallised chloride of calcium.

Nitrous anhydride (or perhaps the acid) may also be prepared by adding a small quantity of ice-cold water to liquid nitric peroxide surrounded by a freezing mixture. After the reaction of the two has taken place, distillation may be effected at a low temperature, and the product condensed in a U-tube immersed in salt and ice.

At 0° and at lower temperatures, nitrous anhydride combines readily with water, forming a blue solution; but at higher temperatures the mixture is decomposed, nitric oxide being given off, and nitric acid remaining in solution. The same decomposition

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takes place when nitrous acid is set free by the action of sulphuric acid on a nitrite. Ice-cold acidified solutions of nitrites however, that of potassium-nitrite with sulphuric acid, for instance, seem to contain undecomposed nitrous acid. Nitrous acid (or perhaps only the moist anhydride) is likewise obtained by the action of nitric acid at a gentle heat on arsenious anhydride:

$$As^2O^3 + 3H^2O + 2HNO^3 = 2H^3AsO^4 + 2HNO^2 \text{ (or } H^2O.N^2O^3\text{)}.$$

Deep-brown vapours are then given off, which when passed over chloride of calcium, give up their water and leave nitrous anhydride. Similar vapours are given off when starch is treated with a large excess of nitric acid, of specific gravity 1·25; but the process is attended with considerable frothing, and occasionally, when a stronger acid is used, with explosion.

Nitrous acid acts very readily both as an oxidising and as a reducing agent. Thus it reduces permanganic and chromic acids to the state of manganous and chromic salts, and mercurous and auric salts even to the metallic state. On the other hand, it bleaches indigo by oxidation, liberates iodine from iodide of potassium, and converts ferrous into ferric salts, with production of nitric oxide.

Nitrous acid decomposes *urea*, with evolution of carbonic anhydride and nitrogen gases:

$$CH^4N^2O + 2HNO^2 = CO^2 + N^4 + 2H^2O.$$

When nitrous acid or the anhydride acts upon a hydrate, either acid, neutral or basylous, it frequently gives rise to the formation of nitroso-compounds, in which an atom of hydrogen is displaced by an atom of nitrosyl, NO: thus with alcohol, $C^2H^5.H.O$, it forms nitrous ether, $C^2H^5.NO.O$. Its reactions with amides and amines are particularly remarkable, and differ according as the amide or amine is present in aqueous or in alcoholic solution:

*a.* An aqueous solution of an amine or amide treated with nitrous acid or anhydride, yields the corresponding acid or alcohol, with evolution of nitrogen: thus

$$\underset{\text{Benzamide.}}{C^7H^5O.H^2.N} + HNO^2 = \underset{\text{Benzoic acid.}}{C^7H^5O.H.O} + H^2O + N^2$$

$$\underset{\text{Phenylamine.}}{C^6H^5.H^2.N} + HNO^2 = \underset{\text{Phenylic alcohol.}}{C^6H^5.H.O} + H^2O + N^2.$$

With larger proportion of nitrous acid, amines yield the corresponding nitrous ethers: thus

$$\underset{\text{Ethylamine.}}{C^2H^5.H^2.N} + 2HNO^2 = \underset{\text{Nitrite of ethyl.}}{C^2H^5NO^2} + 2H^2O + N^2.$$

*b.* When nitrous acid or anhydride is passed into an alcoholic solution of an amine or amide, a different or intermediate reaction takes place, attended with the formation of compounds in which 1 at. nitrogen displaces 3 at. hydrogen. Thus the double molecule of phenylamine reacts with nitrous acid or anhydride according to the following equation:

$$C^{12}H^{14}N^2 + HNO^2 = C^{12}H^{11}N^3 + 2H^2O.$$

In like manner, a double molecule of oxybenzamic acid, $C^7H^7NO^3$, treated with nitrous acid, yields an acid having the composition $C^{14}H^{11}N^3O^6$:

$$C^{14}H^{14}N^2O^6 + HNO^2 = C^{14}H^{11}N^3O^6 + 2H^2O;$$

and similarly for other cases. (See PHENYLAMINES, OXY-ANISAMIC, OXY-BENZAMIC, OXY-CUMENAMIC and OXYTOLUYLAMIC ACIDS.)

Trioxide of nitrogen unites with the tetrachlorides of tin and titanium, forming solid compounds which are obtained by passing the vapour of nitric peroxide into those chlorides. The stannic compound has the composition $SnCl^4.N^2O^3$. (R. Weber, Pogg. Ann. cxviii. 471; Jahresb. 1863, p. 165.)

**Nitrites.** The normal nitrites have the composition $M'NO^2 = \left.\begin{matrix}M'\\NO\end{matrix}\right\}O$ or $M''N^2O^4 = \left.\begin{matrix}M''\\(NO)^2\end{matrix}\right\}O^2$, according as the metal contained in them is mono- or di-atomic. There are also nitrites containing $M^3NO^3 = \left.\begin{matrix}M^3\\NO\end{matrix}\right\}O^2$ or $M''^3N^2O^6 = \left.\begin{matrix}M''^3\\(NO)^2\end{matrix}\right\}O^4$, in which the three atoms of metal denoted by the symbol M may consist of the same or of different metals, including hydrogen: thus there are basic nitrites of lead containing $Pb''^2N^2O^6$ and $Pb''HNO^3$. There are also a few nitrites containing a still larger proportion of base, which may be regarded as compounds of tri-metallic nitrites with oxides or hydrates.

Nitrites are produced: 1. *By the reduction of nitrates.*—When nitrate of potassium or sodium is strongly heated, oxygen is given off, and a mixture of nitrate, nitrite, and free alkali is left; similarly with the nitrates of barium, strontium and others. On dissolving the fused mass thus obtained in water, and adding nitrate of silver, a precipitate of the sparingly soluble nitrite of silver is obtained, which may be purified by solution in water and crystallisation; and from this salt the other nitrites may be formed by double decomposition with the chlorides of the several metals. Nitrate of of lead boiled with metallic lead, yields a basic nitrite of lead, thus:

$$\left.\begin{matrix}\mathrm{Ppb''}\\ \mathrm{(NO^2)^2}\end{matrix}\right\}\mathrm{O^2} + \mathrm{Ppb^2} = \left.\begin{matrix}\mathrm{P\overset{''}{p}b^3}\\ \mathrm{(NO)^2}\end{matrix}\right\}\mathrm{O^4}.$$

2. *By decomposition of nitric peroxide in presence of an alkaline base:*

$$N^2O^4 + H^2O = HNO^2 + HNO^3.$$

When the red vapours, chiefly consisting of pernitric oxide, evolved by distilling fuming nitric acid, are passed into a solution of caustic potash or soda, a mixture of nitrate and nitrite is obtained, from which the nitrous acid may be precipitated in the form of a silver-salt, as above. The same reaction takes place when the vapours evolved on heating starch or arsenious acid with dilute nitric acid are passed into solution of caustic alkali; in this case, however, the vapours contain a considerable quantity of nitrous acid or anhydride, so that a larger proportion of nitrite is obtained.

3. *By oxidation of the lower oxides of nitrogen in presence of bases.*—Nitrite of potassium is formed when oxygen gas is gradually added to nitric oxide standing over caustic potash solution, or when a mixture of 1 vol. oxygen and 4 vol. nitric oxide is passed through the same liquid. Nitrites are also produced by passing nitric oxide over metallic peroxides.

4. *By oxidation of Ammonia.*—Platinum-black quickly converts a mixture of ammonia and atmospheric air into nitrite of ammonium. A coil of heated platinum-wire introduced into a flask of air to which a few drops of strong ammonia have been added, also produces an instantaneous cloud of nitrite of ammonium. Again, when finely divided copper is shaken up with moist ammoniacal air, both the copper and the ammonia are rapidly oxidised and nitrite of copper is formed. Nitrites are frequently found in the well-water of towns, the nitrous acid being probably formed in this case also by oxidation of ammonia.

*Reactions of Nitrites.*—Nitrites are colourless or slightly yellow, and for the most part crystallisable. The solutions of the potassium- and sodium-salts have an alkaline reaction (H. Rose). Nitrites melt when moderately heated and solidify unchanged on cooling; but when strongly heated they are decomposed, giving off nitrogen and oxygen gases. They detonate sharply when heated with combustible bodies. The normal nitrites ($MNO^2$) are all soluble in water, the lead- and silver-salts however are sparingly soluble, so that the solutions of the more soluble nitrites give precipitates with lead- and silver-salts. Heated solutions of nitrites exposed to the air, absorb oxygen and are converted into nitrates. When boiled for a long time in a flask or retort, they are decomposed, yielding a nitrate, nitric oxide and free alkali: *e.g.*,

$$3KNO^2 + H^2O = KNO^3 + 2KHO + 2NO.$$

Nitrites act readily both as reducing and as oxidising agents. Acidulated solutions of nitrites decolorise *permanganate of potassium*, and gradually change the colour of *acid chromate of potassium* to a greenish-blue; they also reduce *trichloride of gold* and *mercurous salts*, giving with the former a brown precipitate of metallic gold, and with the latter a grey precipitate of metallic mercury. These reducing actions distinguish nitrites from nitrates.

In their oxidising action, nitrites resemble nitrates, excepting that they act more readily, and in many cases without the presence of a free acid. Thus they give a dark-brown colour with *ferrous salts* without the addition of acid, whereas nitrates exhibit this effect only when the nitric acid is set free by addition of sulphuric acid. Acidulated solutions of nitrites produce at once a purple colour with *starch* and *iodide of potassium*, whereas pure nitrates do not exhibit this effect until the nitric acid is set free and partially reduced to nitrous acid (p. 85). Nitrites in solution are further distinguished from nitrates by their behaviour with certain metallic salts, giving white precipitates with *lead-* and *silver-salts*, and a yellow precipitate, which forms slowly, with *cobalt-salts* (i. 1045). With aqueous *sulphate of copper*, they produce nitrite of copper which forms a very characteristic apple-green solution.

*Estimation of Nitrous acid.*—Nitrous acid is most correctly determined by oxidation with peroxide of lead, whereby nitrate and hydrate of lead are produced, according to the equation:

$$2PpbO^2 + 2HNO^2 = PpbN^2O^6 + PpbH^2O^2.$$

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A known quantity of the dried peroxide is added to a dilute solution (1 grm. salt in 100 c. c. water) of the nitrite to be analysed, and the solution mixed with acetic acid diluted with 10 or 12 times its bulk of water is warmed for 12 hours to 30° or 40°. The weight of the washed and dried residue gives the quantity of peroxide dissolved, whence the quantity of nitrous acid may be calculated, 1 at. peroxide corresponding to 1 at. nitrous acid. (Péligot. Lang, Jahresb. 1862, p. 581.)

Nitrous acid may be determined volumetrically by means of a standard solution of nitrate of urea, each molecule of that salt, $CH^4N^2O.HNO^3$, decomposing 2 molecules of nitrous acid, according to the equation given on page 70. The solution of nitrate of urea is heated nearly to boiling, and the liquid containing the nitrous acid or the acidulated solution of a nitrite is added drop by drop, till the solution produces a blue colour with starch-paste mixed with iodide of potassium.

Nitrites may also be analysed by several of the methods to be hereafter described for the analysis of nitrates, viz. by igniting the salt with oxide of copper or chromate of lead in a tube the fore part of which is filled with metallic copper, or by the volumetric method with ferrous chloride, the decomposition taking place as represented by the equation:

$$FfeCl^2 + HNO^2 + HCl \cdot = FfeCl^3 + NO + H^2O.$$

Or the acid may be determined by loss, either by simple ignition of the salt, or by decomposing it with sulphuric acid, sal-ammoniac, borax, or silica, &c.

The amount of water in nitrites is best determined by combustion with chromate of lead or oxide of copper, and absorption of the water by chloride of calcium.

### *Metallic Nitrites.*

**Nitrite of Ammonium.** $(NH^4)NO^2.H^2O$.—Obtained by double decomposition of nitrite of lead and sulphate of ammonium, or of nitrite of silver with chloride of ammonium; also by passing nitrous vapours into aqueous ammonia and evaporating over lime. It forms an imperfectly crystallised mass which is resolved by heat into nitrogen and water. Its aqueous solution is similarly decomposed, suddenly if acid, slowly if alkaline.

**Nitrite of Barium.** $Bba''N^2O^4.H^2O$.—Obtained by igniting nitrate of barium at a moderate heat, precipitating the free baryta from the solution of the residue by carbonic acid, mixing the filtrate with alcohol to precipitate the remaining nitrate, and evaporating to the crystallising point (Fischer). Or by passing nitrous vapours into baryta-water, evaporating to dryness, digesting the residue in a small quantity of water, which will dissolve the nitrite of barium and leave the undecomposed nitrate, and evaporating. It is permanent in the air, easily soluble in water and in alcohol, and crystallises according to Fischer, either in needle-shaped hexagonal prisms, or in thick rhombic prisms of $71\frac{3}{4}^\circ$.

**Nitrite of Cadmium,** $Ccd''N^2O^4.H^2O$, is a sparingly soluble laminar mass which decomposes at 100° (Lang, J. pr. Chem. lxxxvi. 295; Jahresb. 1862, p. 99).—According to Hampe (Ann. Ch. Pharm. cxxv. 334; Jahresb. 1863, p. 160), the solution evaporated in a vacuum leaves a viscid, deliquescent mass which when treated with water yields the basic salt $2Ccd''O.N^2O^3$ or $Ccd''O.Ccd''N^2O^4$.

**Nitrite of Calcium.** $Cca''N^2O^4.H^2O$.—Prepared by decomposing a boiling solution of the silver-salt with lime-water, treating the filtrate with sulphydric acid, and then with carbonic acid to remove excess of silver and calcium, and evaporating at a gentle heat. It forms deliquescent prismatic crystals insoluble in absolute alcohol.

**Nitrite of Cobalt.**—Black-brown or red-brown crystals which dissolve in water, and yield a brown precipitate with potash; hence they contain cobaltic oxide (Lang). The solution is decomposed by evaporation, with separation of a basic salt. (Hampe.)

**Nitrite of Cobalt and Potassium.** $\overset{\prime\prime\prime}{Cco}{}^2K^6N^{10}O^{21} = \overset{\prime\prime\prime}{Cco}{}^2O^3.3K^2O.5N^2O^3 = \left.\begin{matrix}\overset{\prime\prime\prime}{Cco}{}^2K^6\\(NO)^{10}\end{matrix}\right\}O^{11}$. *Cobalt-yellow.*—The yellow precipitate formed on adding nitrite of potassium to an acid solution of a cobalt-salt. It is of a very fine colour and is used as a pigment. Its formation serves also as a means of separating cobalt from nickel and many other metals. For the details of its preparation, and the several views of its composition, see Cobalt-yellow (i. 1058).

**Nitrite of Copper.**—Obtained as an apple-green solution by decomposing nitrite of lead with sulphate of copper. It oxidises in the air especially if heated, and is converted into nitrate. According to Hampe, the solution yields by evaporation blue shining laminæ containing $2Ccu''O.N^2O^3$.

**Nitrites of Lead.** *a. Monoplumbic* or *Normal.* $Ppb''N^2O^4 = Ppb''O.N^2O^3$.—Obtained by passing carbonic acid gas through a hot solution of the tetraplumbic salt, till three-fourths of the lead is precipitated as carbonate. The resulting yellow solution evaporated in the air or in a vacuum, deposits the normal salt in long yellow prisms (Péligot), or yellow laminæ (Chevreul), containing 1 at. water according to Nicklès (Compt. rend. xxvii. 244), 2 at. according to Gomès (*ibid.* xxxiv. 187). It is easily decomposible and very soluble in water.

*β. Diplumbic* or *Plumbo-hydric Nitrite.* $2Ppb''O.N^2O^3.H^2O = P\overset{''}{p}bHNO^3$.—Formed in small quantity according to Bromeis (Ann. Ch. Pharm. lxxii. 50), when the yellow diplumbic nitroso-nitrate (*vid. inf.*) is boiled for some time with metallic lead. It is then deposited in long golden-yellow needles.

*γ. Triplumbic.* $3Ppb''O.N^2O^3 = P\overset{''}{p}b^3N^2O^6$.—Deposited when the orange-red nitroso-nitrate is boiled for some hours with lead, in needle-shaped crystals, mostly united in concentric groups having sometimes a fiery-red, sometimes a green colour, but always the same composition (Bromeis, *loc. cit.*). Péligot doubts the existence of this salt.

*Tetraplumbic.* $4Ppb''O.N^2O^3.H^2O$ (Berzelius) $= Ppb''HNO^3.Ppb''O$.—Obtained by boiling a mixture of 1 pt. nitrate of lead and 1½ pt. or more lead with 50 pts. water in a long-necked flask for about 12 hours. It crystallises according to Chevreul in stellate groups of pale flesh-red silky needles; the solution, if quickly cooled, deposits it in the form of a white powder. It gives off its water at 100° (Péligot), together with a small portion of acid (Chevreul); at a red heat it gives off the whole of its acid without fusion (Berzelius). Has a strong alkaline reaction, and dissolves, according to Péligot, in 34·5 pts. boiling and 1250 pts. cold water.

*Nitroso-nitrates of Lead.*—By heating nitrate of lead with metallic lead in certain proportions, salts are obtained which are sometimes regarded as compounds of lead-oxide with nitric peroxide; but they are more probably double salts composed of nitrates and nitrates of lead.

*a.* $2Ppb''O.N^2O^4.H^2O$ or $Ppb''HNO^3.Ppb''HNO^4$.—A solution of normal nitrate of lead in 15 to 20 pts. water heated to 60°—70° for several hours with 63 pts. very finely divided lead, deposits this salt on cooling in straw-yellow shining needles and laminæ having an alkaline reaction, soluble in 85 pts. of cold and 10·6 pts. of boiling water (Bromeis). By prolonged boiling with metallic lead, it is converted into diplumbic nitrate. (Péligot, Bromeis.)

*b.* $7Ppb''O.2NO^4.3H^2O$ or $P\overset{''}{p}b^3N^2O^3.P\overset{''}{p}b^3N^2O^6.P\overset{''}{p}bH^2O^2.2H^2O$.—Obtained by boiling the preceding salt with lead, or a dilute solution of neutral nitrate of lead with 1½ at. metallic iron. Forms hard, orange-red crystals soluble in 1250 pts. of cold and 34 pts. of boiling water. When boiled for some hours with lead, it is converted into triplumbic nitrite (γ) (Péligot, Bromeis). Both these salts (*a*, *b*) are decomposed by baryta-water, yielding nitrate and nitrite of barium. (Péligot.)

*c.* Bromeis, in endeavouring to prepare this salt, once obtained an orange-red but more shining salt, containing, according to his analysis, $3PpbO.N^2O^3 + 4PpbO.N^2O^4 + 3H^2O$.

*d.* The same chemist, by boiling a solution of nitrate of lead for several days with a large excess of metallic lead, obtained light brick-red rhombic crystals, to which he assigned the formula $4PpbO.N^2O^4 + 3PpbO.N^2O^5 + 3H^2O$. For further details on the nitrites and nitroso-nitrates of lead, see *Gmelin's Handbook*, v. 152.

**Nitrite of Magnesium.** $Mmg''N^2O^4.3H^2O$ (Lang); with $2H^2O$ (Hampe).—Laminar deliquescent mass, insoluble in alcohol, easily decomposed by heat; obtained by boiling a solution of the silver-salt with magnesia, removing the excess of silver by sulphydric acid, and evaporating.

**Nitrite of Manganese.**—Deliquescent saline mass.

**Mercuric Nitrite,** $H\overset{''}{h}g^3N^2O^6.H^2O$, separates on evaporating a mixture of mercuric chloride and nitrite of silver. (Lang.)

**Nitrite of Nickel,** $Nni''N^2O^4$, forms reddish-yellow crystals which are permanent in the air, and in the dry state may be heated to 100° without decomposition, but in water only to 80° (Lang). According to Hampe, the solution decomposes even at common temperatures, giving off nitric oxide and leaving a green basic salt, $Noi''O.Nni''N^2O^4$.

**Nitrite of Potassium.** $KNO^2$.—Produced, as already described (p. 70), by heating the nitrate to redness, or by passing nitrous vapours into a solution of caustic potash. When the mixture of nitrate and nitrite thus obtained is dissolved in water, and the solution concentrated, nitrate of potassium crystallises out first, and afterwards the nitrite, but very impure. To obtain a pure salt, Fischer mixes the solution, after the nitrate has crystallised out, with dilute acetic acid and twice its volume of alcohol; more nitrate then crystallises out, and the liquid separates into two layers, the upper consisting of an alcoholic solution of acetate of potassium, the lower of a solution of the nitrite. This solution evaporated over oil of vitriol yields the nitrite in indistinct crystals. Nitrite of potassium may also be obtained pure, by decomposing nitrite of silver with an equivalent quantity of chloride of potassium, or nitrite of lead with carbonate of potassium. Or the following process may be adopted: 1 pt. of nitrate of potassium is fused in an iron crucible, and 2 pts. of lead are added, with constant stirring. The lead oxidises even at a dull red heat; the temperature is then raised to complete the oxidation; the cooled mass is exhausted with water; the solution is treated with sulphide of ammonium to remove a small quantity of lead, then evaporated; and the residue is heated to fusion, to decompose any hyposulphite of potassium that may have been formed (A. Stromeyer, Ann. Ch. Pharm. xcvi. 330). Nitrite of potassium is also formed by the action of ammonia in excess on permanganate of potassium. (Cloez and Guignet.)

Pure nitrite of potassium is a white crystalline, deliquescent, saline mass, neutral to vegetable colours, according to Fischer, alkaline according to H. Rose. When treated with any of the stronger acids, it gives off nitric oxide gas, the nitrous acid eliminated at the first instant being immediately resolved into that compound and nitric acid: $3HNO^2 = HNO^3 + H^2O + 2NO$.

*Double salts of Potassium-nitrite.*—The *barium-salt*, $K^2Bba''N^4O^8.H^2O$, forms long slender needles, permanent in the air, easily soluble in water, insoluble in alcohol. Similar double salts are formed with the nitrites of *strontium*, *calcium*, and *magnesium*, the first being permanent in the air, the other two deliquescent (Lang).—*Cadmium-salts.*—A mixture of cadmium-acetate with excess of potassium-nitrite deposits first the salt $K^2Ccd''N^4O^8$, in oblique, one-sided, shining, yellow prisms; afterwards the salt $K^4Ccd''N^6O^{12}$, in yellow, less lustrous tabular crystals (Lang). Hampe obtained this last salt by recrystallisation, in colourless cubes; the mother-liquor contained another salt which crystallised in prisms, probably $K^2Ccd''N^4O^8$. — The *copper-salt*, $K^6\overset{''}{C}cu^2N^{10}O^{20}.H^2O$, forms thin prisms, black by reflected, dark green by transmitted light, permanent in the air, easily soluble in water, less in alcohol. The solution decomposes easily, depositing dicupric nitrite (Hampe).—*Lead-salts.*—The salt $K^2Ppb''N^4O^8.H^2O$ crystallises in brown-yellow rhombic prisms. A solution of nitrite of lead mixed with a large excess of nitrite of potassium yields long slender prisms less soluble than the preceding, and probably consisting of a compound of the two double salts $K^2Ppb''N^4O^8$ and $K^4Ppb''N^6O^{12}$ (Lang).—The *mercury-salt*, $K^2Hhg''N^4O^8$, forms straw-yellow prisms (Lang).—The *nickel-salt*, $K^4Ni''N^6O^{12}$, forms brown octahedral crystals which dissolve with green colour in water, are insoluble in alcohol, but are decomposed by boiling therewith. A triple salt containing potassium, barium, and nickel, viz. $K^2Bba''Nni''N^6O^{12}$, is obtained by mixing acetate of nickel with potassio-barytic nitrite, or acetate of barium with niccolo-potassic nitrite, in brown-yellow microscopic tablets, sparingly soluble in cold water (Lang, Hampe).—The *palladium-salt* separates from concentrated solutions as a white powder; from more dilute solutions in yellow crystals, very soluble in water. It is decomposed by heat, leaving a residue of palladium and nitrite of potassium (Fischer).—The *silver-salt*, $2KAgN^2O^4.H^2O$, forms yellow rhombic prisms or tablets, permanent in the air, soluble without decomposition in a small quantity of water, decomposed by a larger quantity (Lang, Hampe).—The *zinc-salt*, $K^2Zzn''N^4O^8.H^2O$, crystallises in short, yellow, deliquescent, easily decomposible prisms. (Lang.)

NITRITE OF SILVER. $AgNO^2$.—Obtained by double decomposition of an alkaline nitrite and nitrate of silver. Separates from cold solutions as a white powder composed of capillary crystals; from hot solutions in larger crystals. In small quantities it appears white, in larger quantities yellow. Dissolves in 300 pts. water at ordinary temperatures, easily in boiling water.

NITRITE OF SODIUM. $NaNO^2$.—Prepared like the potassium-salt. Nitrate of sodium is more easily decomposed by heat than nitrate of potassium, and yields a larger proportion of free alkali. In purifying the nitrite by Fischer's method with acetic acid and alcohol (*vid. sup.*), the alcoholic solution does not separate into two layers, and the aqueous alcohol holds in solution acetate and nitrate of potassium, as well as nitrite. It must therefore be evaporated to dryness and the residue exposed to the air. The deliquescent nitrite of sodium may then be decanted, and will yield the crystalline salt by evaporation over oil of vitriol.

The properties of nitrite of sodium are for the most part the same as those of the potassium-salt; it is distinguished however by its greater solubility in alcohol.

NITRITE OF STRONTIUM. $Ssr''N^2O^4$.—Prepared like the barium-salt, but the solution requires to be more strongly concentrated to separate the remaining nitrate. Crystallises in slender needles which slowly deliquesce in damp air.

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**Nitrite of Zinc.**—White laminar mass, consisting of $Zzn''N^2O^4.3H^2O$ (Lang), or $Zzn''O.Zzn''N^2O^4$ (Hampe).

### *Alcoholic Nitrites. Nitrous Ethers.*

**Nitrite of Amyl.** $C^5H^{11}NO^2 = \left.\begin{matrix}NO\\C^5H^{11}\end{matrix}\right\}O$.—Prepared by passing nitrous vapours into amylic alcohol contained in a heated retort, rectifying the distillate, and collecting apart the portion which goes over at 96°. It is a light-yellowish liquid becoming darker while hot, smelling like ethylic nitrite, having a specific gravity of 0·877; boiling at 96° (Balard), at 91° (Rieckher). Its vapour has a reddish-yellow colour, and produces head-ache when inhaled.

It is quickly decomposed by alcoholic potash, yielding nitrite of potassium and probably ethyl-amylic ether; aqueous potash acts but slowly on it. When dropt upon melting potash, it takes fire at the first instant, and forms valerate of potassium. When heated with water in which peroxide of lead is suspended, it yields, according to Riekher, amylic alcohol, nitrate of lead and nitride of lead. (Balard, Ann. Ch. Phys. [3] xii. 318; Rieckher, Jahresb. 1847–8, p. 699.)

**Nitrite of Ethyl.** *Nitrous Ether*, $C^2H^5NO^2$; formerly called *Nitric Ether*, *Salpeter-äther*, *Salpeter-naphtha*, *Ether nitrique*.—This ether was first observed by Rumkel in 1681; but its composition was first exactly determined by Dumas and Boullay (Ann. Ch. Phys. [2] xxxvii. 15). It is produced by the action of nitric or nitrous acid upon alcohol. The action of the former acid is very violent, part of the alcohol being oxidised and the nitric acid reduced to nitrous acid, which then forms nitrous ether with the remaining alcohol.

*Preparation.*—1. A mixture of alcohol and nitric acid (equal parts of alcohol of 35° Bm. and nitric acid of 32°, according to Thénard) is distilled in a retort connected with a series of Woulffe's bottle half-filled with salt-water, heat being applied to set the action going, and the fire afterwards removed. Nitrous ether then collects on the surface of the brine in the form of a light liquid which is to be rectified, and then set aside in contact with quicklime. Berzelius recommends, as originally proposed by Black, to place 8 pts. of fuming nitric acid, 4 pts. water, and 9 pts. alcohol, one above the other in a glass cylinder, leave the whole to itself for two or three days, so that the alcohol and acid may mix slowly by diffusion, and purify the upper layer by distillation.

2. As the direct action of nitric acid upon alcohol is necessarily attended with a considerable loss of alcohol by oxidation, it is more advantageous to reduce the nitric to nitrous acid by means of starch, sugar, &c. Liebig (Ann. Ch. Pharm. xxx. 142) passes the nitrous vapours evolved from nitric acid and starch through cooled dilute alcohol, and condenses the evolved vapours in a cooled receiver. Or equal volumes of alcohol and nitric acid may be distilled with starch or sugar (J. Grant, Pharm. J. Trans. x. 244); or with copper turnings. (E. Kopp, J. Pharm. [3] xi. 320.)

Nitrite of ethyl is a yellowish liquid having an odour of apples, miscible in all proportions with alcohol, but sparingly soluble in water (1 pt. in 48). It boils at 18°. It decomposes by keeping, especially in presence of water, giving off nitric oxide, and often bursting the containing vessel. It is reduced by sulphydric acid or sulphide of ammonium in the manner represented by the equation:

$$\underset{\text{Nitrous ether.}}{C^2H^5NO^2} + 3H^2S = \underset{\text{Alcohol.}}{C^2H^6O} + NH^3 + H^2O + S^3.$$

A solution of ethylic nitrite in alcohol constitutes the *nitric ether* of the pharmacopœias, also called *Sweet Spirits of Nitre*, *Spiritus nitrico-æthereus* or *Spiritus nitri dulcis*.

For details on the preparation and properties of nitrous ether, see *Gmelin's Handbook*, viii. 468.

**Nitrite of Methyl.** $CH^3NO^2$.—Produced by treating wood-spirit with nitric acid and copper turnings or arsenious acid. The less volatile products are condensed in a receiver cooled to 0°, and the gaseous methylic nitrite, after purification by passing through potash-ley, solution of ferrous sulphate, and dry chloride of calcium, is condensed in a tube cooled to between −30 and −40°. As thus obtained it is a liquid of specific gravity 0·991, which boils at −12°, giving off a gas which smells like ethylic nitrite and burns with a green-edged flame. It is also found among the gaseous products evolved on treating brucine with nitric acid. (Strecker, Compt. rend. xxxix. 53.)

### NITRIC PEROXIDE OR TETROXIDE OF NITROGEN. $NO^2$ or $N^2O^4$.

Synonymes: *Nitric Peroxide. Peroxide of Nitrogen. Nitroso-nitric anhydride. Hyponitric acid.* In combination: *Nitryl.*—This is the principal constituent of the orange fumes produced on mixing nitric oxide with oxygen or air. When nitric oxide is mixed with excess of oxygen, 2 vol. of the former combine with 1 vol. of the latter to form 2 vols. of nitric peroxide.

*Preparation.*—1. When a mixture of 2 vols. nitric oxide and 1 vol. oxygen, incorporated by passing through a tube filled with broken porcelain and thoroughly dried by transmission over pumice soaked in oil of vitriol, and then over recently fused slack-potash, is subjected to the action of a freezing mixture of salt and ice, pernitric oxide condenses in transparent crystals, or if the slightest trace of moisture is present, into an almost colourless liquid.—2. Thoroughly dried nitrate of lead heated in a retort, gives off a mixture of pernitric oxide and oxygen gases, the former of which may be condensed as above, while the latter passes on:

$$PpbN^2O^6 = Ppb'O + O + N^2O^4.$$

The first portions of nitric peroxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture, but if the receiver be changed in the midst of the operation, and if every care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

*Properties.*—Pernitric oxide at very low temperatures forms transparent, colourless, prismatic crystals which melt at −9°; but when once melted do not resolidify till cooled down to −30°. Above −9° it forms a mobile liquid of specific gravity 1·451, the appearance of which varies greatly according to the temperature. When still liquid below −9°, it is almost colourless; at −9° it has a perceptible greenish-yellow tint; at 0° the colour is somewhat more marked; at 10° it is decidedly yellow; and at 15° and upwards, orange-yellow, the depth of colour increasing progressively with the temperature up to 22°, the boiling point of the liquid. The vapour has a brown-red colour, the depth of which also increases with the temperature, until at 40° it is so dark as to be almost opaque. This remarkable change of colour is accompanied by a great diminution of density as the temperature rises, both phenomena pointing to a molecular change produced in the vapour by heat. Playfair and Wanklyn (Chem. Soc. J. xv. 156) have determined the density of the vapour by Dumas' method, using nitrogen as a diluent, and find that the densities at different temperatures are as follows:

| Temperature. | Vapour-density. |
|---|---|
| 97·5° | 1·783 |
| 24·5 | 2·520 |
| 11·3 | 2·645 |
| 4·2 | 2·588 |

Now the density required by the formula $NO^2$ for a two-volume condensation is $\frac{14 + 2 . 16}{2} \times 0{\cdot}0693 = 1{\cdot}5893$; that required by $N^2O^4$ for the same condensation is the double of this, viz. 3·1786; and the vapour-densities found by experiment are all intermediate between these two numbers, that found at 97·5° not differing very much from the lower calculated number, while those found at the lower temperatures approach more nearly to that required by the formula $N^2O^4$. Hence it is probable that nitric peroxide exists in two modifications, $NO^2$ and $N^2O^4$, which pass readily one into the other with change of temperature; that at temperatures near 100°, the gas consists chiefly of $NO^2$, at ordinary temperatures of $N^2O^4$, and at intermediate temperatures of mixtures of the two in various proportions. Liquid pernitric oxide gives off at ordinary temperatures an abundance of reddish vapours which when mixed with air are extremely difficult to condense. These vapours have a pungent, suffocating odour and acid taste, are quite irrespirable, and stain the skin of a bright yellow. Concerning the dark bands in the spectrum of lamp-light passing through the vapour of nitric peroxide, see LIGHT (iii. 621).

*Decompositions.*—Nitric peroxide is decomposed by *water*, with production of nitric and nitrous acids, whence it may be regarded as nitroso-nitric anhydride:

$$N^2O^4 + H^2O = HNO^2 + HNO^3.$$

This simple reaction however takes place only at very low temperatures; when a small quantity of ice-cold water is added to pernitric oxide cooled by ice and salt, two layers of liquid are formed, the upper and least coloured of which consists chiefly of aqueous nitric oxide, the lower and darker of nitrous acid or anhydride, which may be distilled off at a low temperature, as already described (p. 74). Pernitric oxide acts in a similar manner upon caustic alkalis when not too dilute, forming a nitrate and nitrite of the alkali-metal. But when nitric peroxide is added to excess of water at ordinary temperatures it is decomposed into nitric acid and the products of decomposition of nitrous acid, namely, nitric acid, water, and nitric oxide gas. As the quantity of nitric peroxide added to the water increases, the evolution of nitric oxide becomes less and less obvious, until, when a considerable quantity of nitric acid has been formed, it disappears altogether. During this saturation of the water with nitric acid, it becomes successively blue, green, and orange-coloured, these colours depending upon the solution of unaltered nitric peroxide in the aqueous nitric acid, which, according to its concentration, is capable of dissolving an increasing quantity, and of decomposing a decreasing quantity of that compound. The similarly coloured liquids produced by treating aqueous nitric acid with nitric oxide gas are thought to owe their colour to the presence of pernitric formed by deoxidation of a portion of the nitric acid:

$$NO + 2HNO^3 = H^2O + 3NO^2.$$

Nitric peroxide is not decomposed at a dull red heat. Mixed nitric peroxide and *oxygen gases* passed over spongy platinum, react upon each other, with production of water and ammonia, the platinum at the same time becoming red-hot. Nitric peroxide is also absorbed by aqueous *sulphydric acid*, with formation of ammonia and deposition of sulphur. Ordinary combustibles are extinguished by nitric peroxide vapour; but *charcoal and phosphorus*, when strongly ignited, burn in it with considerable brilliancy, liberating the nitrogen. It is also decomposed, with liberation of nitrogen, by *iron* and other metals at a red heat. *Potassium* introduced into the vapour at ordinary temperatures inflames spontaneously and burns with a red flame.

*Combinations.*—Nitric peroxide usually reacts with basylous metallic oxides, as before observed, to form nitrates and nitrites; but it has been supposed also to unite directly with some oxides to form definite salts: hence it has been called hyponitric acid. Thus the nitroso-nitrates of lead already described (p. 73) are regarded by Bromeis as compounds of lead-oxide with nitric peroxide; and cobalt-yellow (i. 1058) is by some chemists supposed to have the composition $CoKO.N^2O^4$.

Nitric peroxide, or nitryl, acts as a monatomic chlorous radicle analogous to chlorine and bromine, and capable of displacing one or more atoms of hydrogen in various compounds, chiefly organic, atom for atom; naphthalene, for example, yields the three nitro-derivatives, $C^{10}H^7(NO^2)$, $C^{10}H^6(NO^2)^2$, $C^{10}H^5(NO^2)^3$. Some of these compounds are formed by the direct action of nitric peroxide on organic bodies, *e.g.* mononitronaphthalene, $C^{10}H^7(NO^2)$; but they are generally speaking most easily formed by the action of strong nitric acid (which may itself be supposed to contain the radicle nitryl) on the primary compounds: thus,

$$C^{10}H^8 + \left.\begin{matrix}NO^2\\H\end{matrix}\right\}O = C^{10}H^7(NO^2) + H^2O.$$

Nitric peroxide also unites with amylene, forming *nitrylide of amylene*, $C^5H^{10}(NO^2)$, analogous to the bromide, $C^5H^{10}Br^2$, and possibly also with the other olefines. (Guthrie, see i. 209.)

A chloride of nitryl, $NO^2Cl$, is produced by the action of oxychloride of phosphorus on nitrate of lead; thus,

$$3PbN^2O^6 + 2PCl^3O = Pb^3P^2O^8 + 6NO^2Cl;$$

also by the action of chlorhydro-sulphuric acid upon nitrate of potassium:

$$KNO^3 + HClSO^3 = KHSO^4 + NO^2Cl.$$

It is a thin pale oil smelling somewhat of nitro-muriatic acid. It is decomposed by water into hydrochloric and nitric acids:

$$NO^2Cl + H^2O = HCl + HNO^3.$$

### NITRIC ANHYDRIDE, ACID, AND SALTS.

**Nitric Anhydride,** or **Pentoxide of Nitrogen.** *Anhydrous Nitric acid. Nitrate of Nitryl*, $N^2O^5 = \left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O$.—This compound, discovered by H. Deville in 1849, is produced by decomposing nitrate of silver with chlorine-gas, both being perfectly dry:

$$2AgNO^3 + Cl^2 = 2AgCl + N^2O^5 + O.$$

The nitrate of silver is placed in a U-tube capable of containing about 500 grms. of the salt. This tube is connected with another U-tube of considerable size, and having at the bottom a small spherical reservoir, which serves to receive a very volatile liquid (nitrous anhydride), produced in the course of the operation. The tube containing the nitrate of silver is immersed in water covered with a thin layer of oil and heated by means of a spirit lamp, which communicates with a reservoir kept at a constant level. The chlorine is evolved from a glass gasometer, and its displacement is regulated by a slow and constant flow of sulphuric acid; it is dried by passing over chloride of calcium and then over pumice-stone moistened with sulphuric acid. The bend of the large U-tube is immersed in a freezing mixture. The nitrate of silver is first heated to 180° and deprived of moisture by passing a current of carbonic anhydride through the apparatus. After this, the transmission of the chlorine is commenced. At ordinary temperatures it appears to exert no action; but when the nitrate of silver is heated to 95°, and the temperature then lowered to 58°—68°, the decomposition of the nitrate takes place, chloride of silver being formed and nitric oxygen evolved. At first a portion of nitric peroxide is developed, but as soon as the temperature has reached its lowest point, crystals of nitric anhydride are formed and soon obstruct the U-tube. The gases evolved during the process are coloured; and in the spherical reservoir at the bottom of the tube, there collects a small quantity of liquid which must be removed from the apparatus before transferring the nitric anhydride to another vessel. To effect this transference, the current of chlorine must be replaced by a current of carbonic anhydride, the condensing tube must no longer be cooled; and the bulb destined to receive the crystals must be immersed in a freezing mixture and connected with the U-tube by means of a caoutchouc tube lined with asbestos. The chlorine should pass very slowly, not more than 3 or 4 litres (about 60 cubic inches) in 24 hours. An apparatus arranged as above described will go on day and night without superintendence: it is merely necessary to renew the supply of sulphuric acid which displaces the chlorine, the alcohol which feeds the lamp, and the freezing mixture.

Nitric anhydride forms transparent colourless crystals of great brilliancy, having the form of prisms with six faces and apparently derived from a right rhombic prism. When slowly deposited in a current of the gas strongly cooled, they attain a considerable size. They melt a little above 30°, and boil at about 45°. At 10° the tension of the vapour is very considerable. At temperatures near the boiling point, decomposition appears to begin: hence the tension of the vapour cannot be determined by Dumas' process. (Deville, Ann. Ch. Phys. [3] xxviii. 241.)

**Nitric acid.** $HNO^3 = \left.\begin{matrix}NO^2\\H\end{matrix}\right\}O$ or $H^2O.N^2O^5$.—*Azotic acid. Spirit of nitre. Spiritus nitri acidus. Salpetergeist.* In the dilute state: *Aqua fortis. Eau forte. Scheidewasser.*—This acid has been known from early times. It is mentioned in the writings of Geber in the eighth century; Raymond Lullius, in the thirteenth century, gave directions for preparing it by distilling saltpetre with sulphate of iron; and Glauber soon afterwards obtained it by distilling saltpetre with oil of vitriol, the process by which it is prepared at the present day.

*Formation.*.—1. When nitrogen-gas mixed with 10 or 12 times its bulk of hydrogen is burnt in oxygen, the resulting water is found to contain, in addition to nitrite of ammonium, a small quantity of free nitric acid. Again, when a succession of electric sparks is passed through a moist mixture of 2 vol. nitrogen, and 5 vol. oxygen, traces of nitric acid are slowly formed. It was by a modification of the experiment that Cavendish first ascertained the composition of nitric acid. Davy noticed that traces of nitric acid are produced at the positive pole, when water containing atmospheric air is submitted to electrolysis.

2. By the decomposition of nitrous acid, and of all the oxides of nitrogen. Thus, traces of nitric acid are formed from moist nitrous and nitric oxide gases, by transmission through red-hot tubes, or by electrolisation; while quantities of it are produced by the action of water upon nitrous, nitroso-nitric, and nitric anhydrides. Nitric acid also occurs among the products resulting from the transmission through red-hot tubes of an excess of oxygen mixed with ammoniacal or moist cyanogen gas.

*Preparation.*—1. From *Nitrate of potassium.* 1000 parts of purified saltpetre are distilled in a glass retort with 96 parts of common oil of vitriol, till the residue in the retort becomes tranquil, and no more drops distil over. The ingredients should be but little more than sufficient to half fill the retort, or there will be danger of the mixture boiling over. When a tubulated retort is employed, the oil of vitriol is introduced through the tubulus; but with a plain retort, the acid is poured down the neck by means of a bent tube-funnel, care being taken not to soil the neck with the oil of vitriol. The neck of the retort must reach almost to the middle of the receiver, which is cooled with water, and attached to the retort without any cement.

For every molecule of saltpetre ($KNO^3$ = 101 pts.) 1 molecule of oil of vitriol ($H^2SO^4$ = 98 pts.) is required, in which case 1 molecule of nitric acid passes over, and 1 molecule of acid sulphate of potassium remains in the retort:

$$KNO^3 + H^2SO^4 = KHSO^4 + HNO^3.$$

It was formerly the practice to use only half the quantity of sulphuric acid indicated by the above proportion; and in fact when 1 at. sulphuric acid is heated with 2 at. saltpetre, the whole of the nitric acid is ultimately given off; for the decomposition begins in the manner above indicated, the oil of vitriol acting upon half the quantity of saltpetre present, so that 1 at. nitric acid is disengaged, and a mixture of nitrate and

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acid sulphate of potassium remains behind. This first stage of the reaction takes place at a moderate heat; but afterwards, as the contents of the retort attain a higher temperature, the acid sulphate and nitrate act upon one another, according to the following equation, yielding nitric acid and neutral sulphate of potassium;

$$KHSO^4 + KNO^3 = HNO^3 + K^2SO^4.$$

But these proportions are not advantageous, at least when a colourless acid is required; for at the high degree of heat attained in the latter stage of the process, a great portion of the nitric acid is resolved into oxygen and nitric peroxide, which being absorbed by the acid first distilled over, converts it into red fuming nitric acid.

2. From commercial *Nitrate of sodium* or *Chile saltpetre*.—This salt, on account of its lower price, is now generally used for the preparation of nitric acid on the large scale. The distillation is conducted as above, excepting that 1 molecule (98 pts.) of oil of vitriol is sufficient for the decomposition of 2 molecules (170 pts.) of the nitre (or 58 to 100), because the reaction takes place at a lower temperature than with nitrate of potassium, so that the heat never rises high enough to decompose much of the nitric acid, and the acid collected in the receivers has only a pale yellow colour. If 2 at. sulphuric acid are used to 2 at. nitrate of sodium, the acid must be diluted with one-fourth its weight of water to prevent the mass from boiling over. The best proportions are 100 pts. nitrate of sodium, 116·7 pts. of oil of vitriol and 30 pts. of water; for the acid sulphate of sodium retains not only 1 at. water, like the potassium-salt, but 3 at., which it tends to separate from the nitric acid, so that unless water is added, the mass becomes solid, and the acid is partly resolved into nitric peroxide and oxygen gas. (Wittstein, Repert. Pharm. lxiv. 289.)

Both potash- and soda-nitre generally contain chloride of potassium or sodium, which at the commencement of the process gives rise to the evolution of a yellowish-red mixture of pernitric oxide vapour and chlorine gas. As however the whole of the chlorine passes over at the beginning of the distillation, an acid is at length obtained perfectly free from chlorine; this pure acid amounts to one-half or two-thirds of the whole. It is well to change the receiver as soon as the acid drops, which fall from the neck of the retort, produce but a slight turbidity in a solution of nitrate of silver, and again, when they cease to cause any turbidity whatever. If the saltpetre be purified by repeated crystallisation from every trace of chloride, it yields a perfectly pure acid from the commencement.

The ordinary acid may be purified by distillation with a small quantity of saltpetre —the receiver being changed in the course of the process. Acid containing chlorine passes over first, and afterwards pure nitric acid.

In order to obtain an acid as concentrated and as free as possible from chlorine and nitric peroxide, Millon distils it till a third part has passed over, and then distils the rest with an equal measure of oil of vitriol, the receiver being changed. The latter distillate he purifies, by a second distillation, from the sulphuric acid which comes over; heats the distillate to the boiling point in the bottle in which he intends to preserve it; and passes a continuous current of carbonic anhydride through it, till the acid becomes cold. Should the specific gravity of the acid exceed 1·5, the heating and current of carbonic anhydride must be repeated once or twice, to remove the whole of the nitric peroxide. In this manner, a transparent and colourless acid may be obtained of specific gravity 1·521.

Nitric acid prepared from Chile saltpetre often contains iodine. Such acid, when distilled with sulphuric acid, yields a sublimate of iodine after all the nitric acid has passed over. The iodine (which is in the form of iodic acid) may also be detected by reducing it with sulphydric acid or hyposulphite of sodium and then testing with starch.

Non-volatile impurities, chiefly potassium or sodium salts, are occasionally present in the acid, having been carried over by too rapid distillation.

On the large scale, the potash or soda nitre is distilled in horizontal cast-iron cylinders, or similar vessels, and the acid is condensed in a series of stone-ware Woulffe's bottles, into the last of which a certain quantity of water is poured, to effect complete condensation. Formerly, calcined green vitriol or moistened clay was substituted for sulphuric acid in this process; the greater part of the acid then distilled over as pernitric oxide, which, when condensed by the water, yielded *aqua fortis* (*Scheidewasser*).

In some French manufactories, the generating vessel is connected with a double series of condensers by means of a T-shaped tube fitted with a three-way cock, so that the acid vapours may be made to pass into either set of condensers at pleasure, and shut off from the other. In this way the pure colourless acid which distils over towards the middle of the process may at once be separated from the coloured acid which is given off at the beginning and the end. For full details respecting this and other recent improvements in the methods of distillation and condensation, see *Richardson and Watts's Chemical Technology*, vol. i. pt. 4, pp. 337–350.

The following methods of preparation described by Kuhlmann (Rép. Chim. app.

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1862, p. 337; Wagner's Jahresbericht, 1862, p. 239) may perhaps be advantageously adopted under particular circumstances.

*a.* By heating chloride of manganese with nitrate of sodium, whereby a large quantity of nitrous fumes are given off, and an oxide of manganese is formed which may serve for the evolution of chlorine:

$$5MnCl + 5NaNO^3 = 3MnO.Mn^2O + 5NaCl + 5NO^2 + O.$$

The mixture of nitric peroxide and oxygen coming in contact with the water of the condenser is converted into nitric acid, the excess of nitric peroxide being resolved at the same time into nitric acid and nitric oxide.

*b.* By the action of certain sulphates on the nitrates of potassium and sodium. Sulphate of manganese acts in a similar manner to the chloride; the sulphates of zinc, magnesium and calcium also decompose alkaline nitrates when heated with them.

*c.* By the action of certain metallic oxides, alumina, and silica on nitrates. Wöhler has shown that when a mixture of peroxide of manganese and nitrate of sodium is moderately heated in a close vessel, caustic soda is formed, but no salt of manganic acid, and large quantities of nitrous vapours are given off, which may be condensed in water as above.

*d.* Kuhlmann (Compt. rend. xlvi. 464, 675) recommends the preparation of weak nitric acid, without distillation, by decomposing a strong solution of nitrate of barium (obtained by decomposing nitrate of sodium with chloride of barium) with an equivalent quantity of sulphuric acid. The aqueous nitric acid decanted from the precipitated sulphate of barium has a strength of 10° or 11° Baumé (specific gravity 1·075—1·083), and may be concentrated by boiling to 25° Baumé (specific gravity 1·210).

*Preparation of Fuming Nitric Acid.*—This red fuming liquid, which consists of strong nitric acid holding in solution a considerable quantity of pernitric oxide, and is a much more powerful oxidising agent than the strong colourless acid, is usually prepared by distilling 2 at. saltpetre with 1 at. of sulphuric acid, so as to obtain a residue of neutral sulphate of potassium (p. 79), a considerable portion of the evolved nitric acid being then decomposed by the high degree of heat to which the materials are raised towards the end of the process. It may, however, be more easily obtained by using the ordinary proportions of the ingredients (1 at. nitrate to 1 at. sulphuric acid), and adding a substance capable of reducing the nitric acid to the state of nitrous acid or nitric peroxide: the red acid is then obtained from the very beginning of the process. Sulphur may be used for this purpose, but a small portion of the sulphuric acid formed by its oxidation generally passes over with the nitric acid, and must afterwards be removed by rectification. The following is a better method:—

100 pts. of saltpetre are triturated with 3½ pts. of *starch*, and the mixture is introduced into a retort, and covered with 100 pts. of sulphuric acid of specific gravity 1·85. The beak of the retort is inserted, without luting, into a glass tube 3 or 4 feet long, the farther end of which passes into an ordinary tubulated receiver, which is kept very cool. The distillation begins without external application of heat, requiring only very gentle warming towards the end; 100 pts. of saltpetre yield by this process about 60 pts. of deep red fuming nitric acid. It is best to fill the retort only to about one-third. (Brunner, Rép. Chim. app. iii. 188.)

*Properties.*—Pure nitric acid is a colourless, transparent, mobile liquid, of specific gravity 1·52. It melts at −55° into a buttery mass. It boils at 86°, with partial decomposition, leaving a weaker acid behind. Its vapour-density is 2·258 at 68·5°; 2·373 at 40·5° (Playfair and Wanklyn, Chem. Soc. J. xv. 156): calc. (2 vol.) = 2·183. It exerts a highly corrosive action on organic bodies, and even when somewhat diluted, stains the nitrogenous tissues of a bright orange colour. In the presence of moist air, nitric acid gives off opaque white vapours having a characteristic odour and sour taste. It absorbs water from the air, but with less avidity than sulphuric acid. Its admixture with water is accompanied by a sensible development of heat, and formation of a definite sesqui-hydrate, $2HNO^3.3H^2O$, which is a colourless strongly acid liquid having a specific gravity of 1·42, containing 60 per cent. of nitric anhydride or 70 per cent. $HNO^3$, and boiling according to Millon at 123°, under the ordinary atmospheric pressure. Weaker and stronger acids are alike reduced to this state of hydration by boiling, the weaker acids losing water and the stronger acids the elements of nitric anhydride. According to Roscoe, however (Chem. Soc. Qu. J. xiii. 150), aqueous nitric acid, which boils constantly under the ordinary pressure, contains 68 per cent. $HNO^3$, which cannot be represented by any simple atomic proportion; moreover, as with hydrochloric acid (i. 892) and other acids, the composition of nitric acid of constant boiling-point varies with the pressure under which the ebullition takes place.

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*Table showing the strength of Aqueous Nitric acid according to its Specific Gravity at* 15·5° C. *or* 60° F. (Ure.)

| Specific gravity. | $N^2O^5$ in 100 pts. by weight. | Specific gravity. | $N^2O^5$ in 100 pts. by weight. | Specific gravity. | $N^2O^5$ in 100 pts. by weight. | Specific gravity. | $N^2O^5$ in 100 pts. by weight. |
|---|---|---|---|---|---|---|---|
| 1·5000 | 79·700 | 1·4189 | 59·775 | 1·2947 | 39·850 | 1·1403 | 19·925 |
| 1·4980 | 78·903 | 1·4147 | 58·978 | 1·2887 | 39·053 | 1·1345 | 19·128 |
| 1·4960 | 78·106 | 1·4107 | 58·181 | 1·2826 | 38·256 | 1·1286 | 18·331 |
| 1·4940 | 77·309 | 1·4065 | 57·384 | 1·2765 | 37·459 | 1·1227 | 17·534 |
| 1·4910 | 76·512 | 1·4023 | 56·587 | 1·2705 | 36·662 | 1·1168 | 16·737 |
| 1·4880 | 75·715 | 1·3978 | 55·790 | 1·2644 | 35·865 | 1·1109 | 15·940 |
| 1·4850 | 74·918 | 1·3945 | 54·993 | 1·2583 | 35·068 | 1·1051 | 15·143 |
| 1·4820 | 74·121 | 1·3882 | 54·196 | 1·2523 | 34·271 | 1·0993 | 14·346 |
| 1·4790 | 73·324 | 1·3833 | 53·399 | 1·2462 | 33·474 | 1·0935 | 13·549 |
| 1·4760 | 72·527 | 1·3783 | 52·602 | 1·2402 | 32·677 | 1·0878 | 12·752 |
| 1·4730 | 71·730 | 1·3732 | 51·805 | 1·2341 | 31·880 | 1·0821 | 11·955 |
| 1·4700 | 70·933 | 1·3681 | 51·068 | 1·2277 | 31·083 | 1·0764 | 11·158 |
| 1·4670 | 70·136 | 1·3630 | 50·211 | 1·2212 | 30·286 | 1·0708 | 10·361 |
| 1·4640 | 69·339 | 1·3579 | 49·414 | 1·2148 | 29·489 | 1·0651 | 9·564 |
| 1·4600 | 68·542 | 1·3529 | 48·617 | 1·2084 | 28·692 | 1·0595 | 8·767 |
| 1·4570 | 67·745 | 1·3477 | 47·820 | 1·2019 | 27·895 | 1·0540 | 7·970 |
| 1·4530 | 66·948 | 1·3427 | 47·023 | 1·1958 | 27·098 | 1·0485 | 7·173 |
| 1·4500 | 66·155 | 1·3376 | 46·226 | 1·1895 | 26·301 | 1·0430 | 6·376 |
| 1·4460 | 65·354 | 1·3323 | 45·429 | 1·1833 | 25·504 | 1·0375 | 5·579 |
| 1·4424 | 64·557 | 1·3270 | 44·632 | 1·1770 | 24·707 | 1·0320 | 4·782 |
| 1·4385 | 63·760 | 1·3216 | 43·835 | 1·1709 | 23·900 | 1·0267 | 3·985 |
| 1·4346 | 62·963 | 1·3163 | 43·038 | 1·1648 | 23·113 | 1·0212 | 3·188 |
| 1·4306 | 62·166 | 1·3110 | 42·241 | 1·1587 | 22·316 | 1·0159 | 2·391 |
| 1·4269 | 61·369 | 1·3056 | 41·444 | 1·1526 | 21·519 | 1·0106 | 1·594 |
| 1·4228 | 60·572 | 1·3001 | 40·647 | 1·1465 | 20·722 | 1·0053 | 0·797 |

The numbers in this table were obtained by mixing known weights of water and nitric acid of specific gravity 1·500, which was regarded by Ure as the strongest acid corresponding to the formula $H^2O.N^2O^5$; but as the true specific gravity of this acid is 1·52, the numbers probably require some correction.

*Reactions.*—Nitric acid, especially when heated, is a most powerful oxidising agent, and acts more or less violently on all the solid non-metallic elements, converting *iodine, sulphur, selenium, tellurium, phosphorus, arsenic, boron, carbon,* and *silicon,* into iodic, sulphuric, selenious, tellurous, phosphoric, arsenic, boric, carbonic, and silicic acids respectively; also upon all metals excepting tantalum, titanium, gold, platinum, and some of its congeners. Most metals are converted by it into nitrates, but *tin, antimony,* and *tungsten,* when heated with the moderately strong acid, are oxidised into the insoluble stannic, antimonic, and tungstic anhydrides. The degree of reduction which the nitric acid sustains in these reactions varies according to the substance acted upon, and according to the strength and temperature of the acid. In most cases, nitric oxide is set free, and forms red fumes of nitric peroxide on coming in contact with the air: hence nitric acid may generally be recognised by the red fumes which it evolves on coming in contact with metals or other oxidable bodies. The reaction with *copper* already described (p. 68), may be regarded as typical of the ordinary action of nitric acid on metals. In some cases, however, other oxides of nitrogen are evolved. Finely divided *charcoal,* drenched with strong nitric acid, at a temperature below 0°, is not oxidised, but decomposes the nitric acid, with evolution of nitric peroxide and free oxygen (Schönhein). *Silver* and *palladium* dissolved in nitric acid without heat, liberating nitrous anhydride, or nitrous acid, which remains in solution, so that the reaction takes place without evolution of gas. Nitrous anhydride is also produced when *arsenious anhydride* is dissolved in nitric acid. *Zinc, tin,* and *iron* dissolve in the cold dilute acid, with production of nitrous oxide, $N^2O$; but if a stronger acid is used, or the temperature rises, nitric oxide is evolved. Free nitrogen also occurs among the products of the violent action of nitric acid on several of the metals. Thus, when *copper* is dissolved in moderately strong nitric acid, at an increased temperature, the evolved nitric oxide gas is contaminated with nitrogen; whereas, when it is dissolved in weak acid, at a low temperature, the gas is contaminated with nitrous oxide. Nitrogen is also set free when strong nitric acid is decomposed by red-hot charcoal. The action on zinc, tin, iron, and several other metals, is attended with formation of ammonia; thus:

$$9HNO^3 + 4Zzn = 4Zzn''N^2O^6 + 3H^2O + H^3N.$$

Nitric acid converts *arsenites* into arsenates, *ferrous* into ferric, and *stannous* into stannic salts. In the concentrated state, it rapidly oxidises *sulphurous* into sulphuric acid, and *sulphydric* acid into water and pure sulphur; but with weak nitric acid, free from nitrous acid, this action is very gradual; indeed, pure nitric acid is altogether a less powerful oxidiser than that which contains nitrous acid or nitric peroxide in solution.

*Hydriodic* acid and the *iodides* are decomposed by nitric acid, with liberation of iodine and nitric oxide:

$$3HI + HNO^3 = 2H^2O + I^2 + NO.$$

*Hydrochloric* and nitric acids, heated together, decompose one another, yielding dichloride of nitrosyl, water, and free chlorine:

$$3HCl + HNO^3 = NOCl^2 + 2H^2O + Cl.$$

Nitric acid acts with great energy on most *organic bodies*, the kind of action varying according to the strength of the acid and the temperature. Dilute or moderately strong nitric acid generally exerts an oxidising action, especially if the temperature is allowed to rise, the final products being in most cases oxalic, formic, and acetic acids, or if the action be pushed to the utmost, carbonic anhydride and water: picric acid is also a frequent ultimate product; resinous bodies are frequently converted by nitric acid into succinic acid. The intermediate products are very numerous, varying according to the substance acted upon: indigo $C^8H^5NO$, yields isatin $C^8H^5NO^2$; sugar yields saccharic acid; gum and milk-sugar yield mucic acid: oleic acid yields a number of acids of the series $C^nH^{2n}O^2$, and $C^nH^{2n-2}O^4$ (see *Gmelin's Handbook*, vii. 122). The strongest pure nitric acid, especially if rise of temperature be prevented, acts for the most part in a different way, displacing one or two atoms of hydrogen in the compound, and introducing an equal number of atoms of nitryl, $NO^2$, in their place: thus with benzene, $C^6H^6$, it forms nitrobenzene, $C^6H^5(NO^2)$; with *phenol*, $C^6H^6O$; nitrophenol, $C^6H^5(NO^2)O$, dinitrophenol, $C^6H^4(NO^2)^2O$, and trinitrophenol or picric acid, $C^6H^3(NO^2)^3O$; with *cellulose*, $C^6H^{10}O^5$, it forms trinitro-cellulose, $C^6H^7(NO^2)^3O$, &c.

The industrial uses of nitric acid depend upon both these modes of action. It is the most frequent solvent of metals, and is used by engravers for etching designs on copper-plates; also for etching on steel and stone. The cleansing of copper and bronze, the refining and assaying of gold and silver, the preparation of the nitrates of copper, silver, and mercury, and numerous analytical operations connected with manufactures, depend also upon the oxidising and solvent action of nitric acid. A mixture of nitric and hydrochloric acids forms *aqua regia* or *nitro-muriatic acid*, used for dissolving gold, platinum, and other metals, and alloys not attacked by nitric acid alone. The preparation of oxalic acid and of picric acid, now extensively used as a yellow dye for silk, likewise depends upon the oxidising action of nitric acid. This last substance is however likewise formed, as above mentioned, by the action of very strong nitric acid on phenol or carbolic acid, which is an action of substitution. The preparation of nitrobenzene for the manufacture of aniline, and that of gun-cotton, are also industrial applications of nitric acid of daily increasing importance.

**Nitrates.** The normal nitrates are monometallic, *e.g.* nitrate of potassium $KNO^3$, nitrate of copper $Cu''N^2O^6$, nitrate of bismuth $Bi'''N^3O^9$, the general formula being $R_{(n)}N^nO^{3n}$ or $R_{(n)}O^n.nN^2O^5$, the symbol $R_{(n)}$ denoting an *n*-atomic radicle. There are also basic nitrates, most of which are derivable from the normal nitrates by addition of 1 or 2 molecules of oxide, and may be represented by the general formula $R_{(n)}{}^3N^nO^{4n}$; *e.g.*

| | |
|---|---|
| Basic nitrate of Mercurosum . . | $\overset{\prime}{H}hg^2HNO^4 = HhgNO^3.HhgHO$ |
| Basic nitrate of Mercuricum . . | $\overset{\prime\prime}{H}hg^3N^2O^8 = Hhg''N^2O^6.2Hhg''O$ |
| Basic nitrates of Lead . . . | $\overset{\prime\prime}{Pb}{}^3N^2O^8 = Pb''N^2O^6.2Pb''O$ |
| | $\overset{\prime\prime}{Pb}{}^2H^2N^2O^8 = Pb''N^2O^6.Pb''H^2O^2$ |
| Basic nitrate of Bismuth . . . | $\overset{\prime\prime\prime}{Bi}{}^3N^3O^{12}$<br>or $\overset{\prime\prime\prime}{Bi}NO^4$ $= Bi'''N^3O^9.\overset{\prime\prime\prime}{Bi}{}^2O^3.$ |

These basic nitrates might be called orthonitrates, being related to the normal nitrates in the same manner as the orthophosphates, $R_{(n)}P^nO^{4n}$, to the metaphosphates, $R_{(n)}P^nO^{3n}$; they are, however, the exceptional salts, whereas amongst the salts of phosphoric acid, the orthophosphates are the ordinary, and the metaphosphates the exceptional salts.

*Occurrence and formation of Nitrates.*—Several nitrates occur in nature. Nitrate of sodium, or cubic nitre, exists in distinct layers or beds beneath the superficial soil in many parts of Chile and Peru. Nitrate of potassium, or prismatic nitre, occurs as an efflorescence on the surface of the soil in various parts of India, especially in the district of Tirrhût in Bengal. Nitrate of calcium is produced artificially in several countries of Europe by mixing decomposing vegetable and animal matters with cinders, chalk, marl, &c., moistening the masses repeatedly with urine, exposing them freely to the air for two or three years, and lixiviating. A similar formation of nitrates occurs in the so-called *saltpetre rot*, or efflorescence which sometimes occurs upon the old walls of stables and other badly drained buildings. Nitrates are formed wherever nitrogenised organic matters in contact with earthy carbonates or other bases are freely acted upon by the air. Lumps of chalk moistened with weak ammonia and exposed to the air have been found to yield nitrate of calcium; but it is doubtful whether the production of ammonia is a necessary stage in the process of nitrification. The shallow well-waters of towns nearly always contain nitrates, from contamination with sewer or cesspool drainage, &c. But many natural waters obtained from strata containing very little organic matter have also been found to contain nitrates. Hence it has been inferred that these salts might be produced directly from the free nitrogen and oxygen gases dissolved in the water, the porous beds through which it filters serving to effect the combination by an action resembling that of spongy platinum. It must be borne in mind, however, that rain-water always contains carbonate and nitrate of ammonium, and that these ammoniacal salts may be the real sources of the nitrates found in the waters. Nitrates are found in the juices of plants, particularly in those with large fleshy tuberose roots, and are probably acquired from the soil by direct imbibition.

The nitrates of potassium and sodium are obtained in a state of purity by frequently recrystallising the native salts. Nitrate of potassium is also obtained by decomposing crude nitrate of calcium with wood-ashes, and by decomposing nitrate of sodium with chloride of potassium. The other metallic nitrates are prepared by dissolving different metals, their hydrates, oxides, or carbonates in aqueous nitric acid, and crystallising by evaporation.

*Properties.*—Most nitrates are crystalline salts. The normal nitrates are all soluble in water; their solutions are for the most part neutral, and have a cooling saline taste. The crystallised nitrates of ammonium, potassium, sodium, barium, strontium, lead, and silver are anhydrous; that of mercurosum is monohydrated, $Hhg'NO^3.H^2O$; those of cadmium, calcium, and probably strontium are tetrahydrated, *e.g.* $Cca''N^2O^6.4H^2O$; and those of magnesium, zinc, cobalt, nickel, iron, manganese, copper, and uranyl, hexhydrated, *e.g.* $Ccu''N^2O^6.6H^2O$. Copper also forms a trihydrated salt, $Ccu''N^2O^6.3H^2O$. Most nitrates fuse readily, and all decompose when strongly heated. The nitrates of the highly basylous metals at first give off nearly pure oxygen, and are converted into nitrites, afterwards a mixture of oxygen and nitrogen gases, together with some nitric peroxide. Other nitrates, which decompose at a lower temperature, those of mercury, lead, and silver, for instance, evolve a mixture of nitric peroxide and oxygen. A few still more easily decomposible hydrated salts, the trinitrates of aluminium and bismuth, for instance, evolve unaltered nitric acid. Ignited nitrate of silver leaves a residue of metallic silver; but most normal nitrates when strongly heated, leave residues of oxide analogous in composition to original salt; thus cupric nitrate, $Cu''N^2O^6$, leaves cupric oxide, $Cu''O$; tri-nitrate of bismuth, $Bi'''N^3O^9$. leaves trioxide of bismuth, $Bi'''^2O^3$; ferrous and manganous nitrates, however, leave oxides richer in oxygen than those which correspond to the original salts, viz. $Ffe^2O^3$ and $Mmn^3O^4$. Nitrates heated with combustible bodies produce a more or less violent deflagration or explosion. The acid-forming bodies, metallic or non-metallic, when deflagrated with nitre, leave potassium- or sodium-salts of their respective acids; *e.g.* selenium ignited with nitrate of potassium forms selenate of potassium, $K^2SeO^4$; manganese yields manganate of potassium, $K^2Mmn''O^4$.

*Reactions serving for the detection of Nitric acid.*—1. All nitrates are decomposed by *sulphuric acid*, with liberation of nitric acid, the fumes of which produce a purple discoloration on *starch-paper* moistened with iodide of potassium.—2. In contact with metallic *copper* (wire or turnings) the nitric acid is reduced to nitric oxide, which forms orange-coloured fumes in the vessel above the liquid.—3. Sulphuric acid to which a fragment or solution of a nitrate is added, acquires the property of bleaching *indigo*.—4. When a solution of a nitrate is mixed in a test-tube with strong sulphuric acid, the mixture left to cool, and a strong solution of *ferrous sulphate* or *chloride* continually poured upon it, so as to float on the surface, the iron solution quickly acquires a dark-brown colour arising from the formation of the compound of nitric oxide with the ferrous salt already mentioned (p. 69). If only a very small quantity of nitrate is present, a rose-coloured, purplish-brown, or dark brown ring is formed at the surface of contact of the two liquids. This reaction is extremely delicate; in applying it, however, care must be taken to cool the liquid before pouring in the iron solution, because the dark brown compound is decomposed by heat, nitric oxide being evolved and the colour destroyed.—5. When a solution of a nitrate is mixed with a few drops of *ferrocyanide of potassium*, then with a small quantity of hydrochloric acid, the liquid heated to 71°, and slightly supersaturated on cooling with an alkaline carbonate, a nitroferricyanide of alkali-metal (ii. 250) is formed, and the filtered liquid, when mixed with a few drops of *sulphide of ammonium* or other alkaline sulphide, exhibits a transient purple or violet colour (E. W. Davy, Chem. Gaz. 1850, p. 219).—6. Nitrates heated with excess of *hydrochloric acid* give off chlorine, which may be recognised by its odour and its bleaching powers; also by the power which the solution acquires of dissolving gold leaf.

7. When nitrate of potassium or sodium is heated with *zinc*, *water*, and excess of *potash*, ammonia is evolved, its formation arising from the union of the nitrogen contained in the salt with the hydrogen evolved by the action of the zinc on the potash-solution. This method does not, however, effect a complete decomposition of the nitric acid; and if applied to a liquid containing only small quantities of that acid, would not give certain indications. But it may be greatly facilitated and rendered complete, by the introduction of another metal not acted upon by the potash, so as to form a voltaic circuit. Thus, when zinc and iron are placed together in a moderately strong solution of caustic potash, hydrogen is freely disengaged, even without the application of heat, the zinc being oxidised and the hydrogen evolved at the surface of the iron. A similar effect is observed if platinum, copper, or tin be substituted for the iron; but with these metals the action is less energetic. The addition of a nitrate to the liquid is followed by an immediate evolution of ammonia. To apply this reaction to the detection of nitric acid, the liquid to be examined is reduced to a small bulk and poured into a test-tube containing 2 or 3 grammes of a mixture of granulated zinc and clean iron-filings. A small quantity (5 or 6 cub. cent.) of strong potash-solution is then added, and the whole is heated to boiling. Ammonia may then be detected at the mouth of the tube by its usual characters, viz. its odour, its alkaline reaction, and the formation of dense white fumes when a rod dipped in dilute hydrochloric acid is held near the mouth of the tube; 5 milligrammes of nitre thus treated give a distinct reaction with reddened litmus. The delicacy of the test may be greatly increased by the use of *potassio-iodide of mercury* (the solution obtained by adding iodide of potassium to corrosive sublimate till the scarlet precipitate first formed just redissolves), which produces a red or brown precipitate, according to the quantity of ammonia present. The mixture should be gently heated, and the evolved gases passed into a small quantity of dilute hydrochloric acid. The acid solution is then to be supersaturated with potash, and tested with a drop of potassio-iodide of mercury; 0·001, 0·0005, and even 0·0001 gramme of saltpetre thus treated gives a distinct red coloration (A. Vernon Harcourt, Chem. Soc. J. xv. 381). Schulze (Chem. Centralblatt, No. 53) proceeds in a similar manner, but uses platinised zinc in place of the mixture of zinc and iron.

This method, which may be used also for the quantitative estimation of nitric acid (p. 89), serves to distinguish that acid from all others excepting nitrous acid.

8. Strong nitric acid converts *phenol* (or carbolic acid) into reddish-brown nitro-phenol. To apply this reaction to the detection of nitric acid, 1 pt. of phenol is dissolved in 4 pts. of strong sulphuric acid, and the solution is diluted with 2 pts. of water. The substance to be tested, if in solution, is evaporated on a porcelain crucible or its cover, and a drop or two of the phenyl-sulphuric acid is allowed to fall upon it at a temperature of about 100°. If nitric acid is present, a reddish-brown colour is immediately produced. This test is said to be more delicate than that with ferrous sulphate, having given a distinct indication of the presence of nitric acid in the residue of a drop of water not containing more than 0·000006 gramme of saltpetre, whereas four such drops were not sufficient to give a perceptible indication with the iron test. If organic matters, or compounds of chlorine, bromine, or iodine are likewise present, from which sulphuric acid would separate carbon or the haloïds, it is best to add a drop or two of strong ammonia to the coloured product, when the haloïds will be dissolved in the form of colourless salts, and the carbon will remain suspended in small particles, not interfering with the recognition of the characteristic yellow colour of nitrophenylate of ammonium. (H. Sprengel, Chem. Soc. J. xvi. 396.)

All the reactions above described are exhibited by nitrous as well as by nitric acid, and even with greater facility, for the nitrites are more easily decomposible than the nitrates, and nitrous acid, though it contains less oxygen, is a more powerful oxidising agent than nitric acid. The nitrites are however distinguished from nitrates by the reactions already described (p. 71). According to D. Price (Chem. Soc. J. iv. 251), nitric acid free from nitrous acid does not decompose iodide of potassium or produce a brown coloration with ferrous salts, or decolorise indigo, these effects being produced only after a portion of the nitric acid has been reduced to nitrous by warming with sulphuric acid. The reactions with indigo and hydrochloric acid (3 and 6) are likewise produced by the oxygen-salts of chlorine, bromine and iodine, but these salts are easily distinguished from nitrates and nitrites by the fact that they leave when ignited a residue of chloride, bromide, or iodide of silver; also by their reaction with nitrate of silver and many others.

### *Quantitative Analysis of Nitrates. Estimation of Nitric acid.*

I. Gravimetric methods. 1. *By neutralisation with Baryta.*—The quantity of free nitric acid in an aqueous solution may be determined by agitating the liquid with carbonate of barium till the acid is completely neutralised, then filtering, evaporating to dryness, taking care not to heat the residue too strongly, and weighing the dry nitrate of barium thus obtained. 100 parts of this salt correspond to 41·39 parts $N^2O^5$, and 48·28 parts $H^2N^2O^6$.

Or, the solution of nitrate of barium may be decomposed by sulphuric acid, the precipitated sulphate of barium weighed, and the equivalent quantity of nitric acid thence determined. 100 parts $Ba^2SO^4$ = 46·35 parts $N^2O^5$, and 54·08 parts $H^2N^2O^6$.

If the solution of nitric acid is very dilute, so that it decomposes carbonate of barium but slowly, it is better to neutralise with baryta-water, then pass carbonic anhydride through the liquid, to remove any excess of baryta, filter, and treat the filtered solution of nitrate of barium as above.

When nitric acid is combined with a base, it may be liberated by distilling a solution of the salt with sulphuric acid, in the proportion of at least 1 at. sulphuric acid ($H^2SO^4$) to 1 at. of the nitrate. The mixture, which should be rather dilute, is distilled from a tubulated retort into a receiver provided with efficient means of condensation, the distillation being carried nearly to dryness. After the residue has cooled, more water is added, and the distillation is repeated with a fresh receiver. The quantity of nitric acid in the united distillates is then determined by neutralisation with baryta, as before. With the proportion of sulphuric acid above indicated, and a considerable quantity of water, there is no reason to fear the reduction of any portion of the nitric acid to a lower oxide of nitrogen.

The residue in the retort serves for the estimation of the base. In the case of the stronger bases, viz. the alkalis and alkaline earths, whose sulphates can sustain a red heat without decomposition, this residue may be heated till all the excess of sulphuric acid is driven off, the expulsion of the last portions being facilitated by placing a piece of carbonate of ammonia in the crucible. A neutral sulphate then remains, from which the quantity of base may be calculated, and this, deducted from the total weight of the anhydrous nitrate, gives also the quantity of nitric anhydride. The weaker bases whose sulphates are decomposed by ignition, must be determined by precipitation in the manner specially adapted to each.

The following methods of separating nitric acid from bases may also be adopted in particular cases.

Nitrates whose bases are precipitated by baryta-water and are insoluble in excess of that reagent, may be analysed by boiling them, either in the solid state or in solution, with excess of baryta-water, then filtering, removing the excess of baryta by carbonic anhydride, and determining the quantity of nitrate of barium in the filtrate as above.

Some nitrates, as those of lead, copper, bismuth, &c., may be decomposed by sulphydric acid, the metal being precipitated as sulphide, care being taken to dilute the solution and not to use a large excess of sulphydric acid: otherwise sulphur may be precipitated, and part of the nitric acid converted into ammonia. The filtrate, containing the whole of the nitric and a small quantity of sulphydric acid, is mixed with baryta-water; a stream of carbonic anhydride is then passed through it, to precipitate the excess of baryta and expel the sulphydric acid; the liquid again filtered; and the filtered solution of nitrate of barium treated as above.

In other cases, the bases may be precipitated by an alkaline sulphide, best with sulphide of barium. The liquid filtered from the precipitated metallic sulphide then contains nitrate of barium and excess of sulphide of barium, and may be treated in the manner just described.

From nitrate of barium, the base may be precipitated by sulphuric acid; from the nitrates of strontium and calcium, by sulphuric acid and alcohol. The filtrate is neutralised with baryta-water, and the nitric acid determined as above.

From the nitrates of ammonium, potassium, sodium, lithium, and magnesium, the acid is most easily separated by distillation with sulphuric acid, as already described.

2. *By the loss of weight sustained by Nitrates on ignition.*—All nitrates are decomposed by heat, the nitrogen being wholly, the oxygen sometimes partly and sometimes wholy expelled, and the base remaining either as an oxide or as metal. Silver, palladium, and other noble metals are left in the metallic state when their nitrates are heated to redness; lead, bismuth, copper, cadmium, zinc, nickel, magnesium and one or two of the rarer metals, remain as protoxides, $M''O$. In the former case, if the salt is anhydrous, the loss of weight sustained on ignition consists of $N^2O^6$, in the latter of $N^2O^5$; but in many cases, as with the proto-salts of iron, cobalt, and manganese, the result is complicated by the formation of an oxide of higher degree of oxidation than that which may be supposed to exist in the original salt. The nitrates of the alkali-metals and alkaline-earth-metals part with the whole of their nitric anhydride when very strongly ignited, leaving the bases $M^2O$ or $M''O$; but these bases can scarcely be prevented from absorbing small quantities of carbonic acid from the air during the process, or as they cool; moreover, they attack all vessels in which the ignition can be performed, uniting partly with their substance; hence the amount of acid in these nitrates cannot be conveniently determined by ignition.

According to **Schaffgotsch**, the amount of acid in a nitrate may be easily determined by igniting a finely pulverised mixture of the salt with anhydrous borax in a platinum crucible, taking care to raise the heat gradually. The loss of weight then gives the amount of nitric anhydride.

**Reich** (J. pr. Chem. lxxxiii. 262) estimates the amount of nitric acid in alkaline nitrates by igniting them, mixed with from 4 to 6 times their weight of pounded quartz; the loss of weight then also gives directly the quantity of anhydride, $N^2O^5$.

3. *By conversion of nitrates into chlorides.*—The nitrates of the alkali-metals and alkaline-earth-metals may be converted into neutral chlorides, of perfectly definite composition, by igniting them in a covered platinum crucible with excess of chloride of ammonium, as long as fumes of sal-ammoniac continue to escape, the operation being repeated till the weight of the residual chloride becomes constant. The quantity of base is then determined by calculation, and from this, the quantity of nitric acid in the salt.

The chlorides of most of the heavy metals suffer partial decomposition when ignited, especially in contact with moisture.

4. *By the action of Arsenious anhydride.*—Nitric acid converts arsenious into arsenic anhydride, according to the equation,

$$As^2O^3 + 2HNO^3 = As^2O^5 + 2HNO^2.$$

Hence for every molecule of arsenic anhydride produced, two molecules of nitric acid ($HNO^3$) must be decomposed. To apply this reaction to the estimation of nitric acid, the salt to be analysed (which must not contain lime or phosphoric acid) is mixed with three times its weight of arsenious anhydride; the whole dissolved in strong hydrochloric acid; the solution evaporated to dryness; ammonia added in excess; and the arsenic precipitated by addition of sal-ammoniac and sulphate of magnesium, as *ammonio-magnesian arseniate*, which, when dried at 100°, has the composition $(NH^4)^2\overset{''}{M}g^2As^2O^8.H^2O$. From the weight of this salt, the amount of nitric acid is calculated by the proportion,

$$(NH^4)^2\overset{''}{M}g^2As^2O^8.H^2O : 2HNO^3 = 372 : 126.$$

*Estimation of Water in Nitrates.*—In the hydrated nitrates of the stronger bases, the amount of water is easily determined by heating them to 100°, the water being then completely expelled without any loss of acid. But the nitrates of the weaker bases cannot bear this temperature without decomposition, and in these the water must be determined at the same time as the nitrogen, by igniting the nitrate in a combustion-tube, at the open end of which is placed a quantity of copper turnings, and attaching to the combustion-tube a drying tube containing chloride of calcium, in the same manner as for organic analyses. On heating the tube, the water and nitric anhydride are driven off; the water collects in the chloride of calcium tube, the increase of weight of which determines its quantity; and the nitric anhydride is reduced by the red-hot copper to pure nitrogen, which passes on and may be collected over mercury and measured.

*Separation of Nitrates from Chlorides.*—All chlorides containing metals which form insoluble phosphates, may be separated from nitrates by heating the solution containing them with phosphate of silver. A trace of that salt, which remains in solution, may be easily determined, and in some cases separated by means of alcohol. Lassaigne has employed this method for separating the chlorides of magnesium and calcium from the corresponding nitrates in well-waters.

In some cases, carbonate of silver is a more convenient precipitant than the phosphate, especially for separating the chlorides of the alkaline earth-metals and of magnesium from the corresponding nitrates. In other cases, however, the carbonate cannot be used, because a great number of oxides are precipitated by it.

The chlorides of the alkali-metals cannot be separated from the nitrates by this method, because the phosphates of those bases are soluble. The method most generally adopted for estimating the quantity of chlorides contained in alkaline nitrates, especially in crude saltpetre, is to precipitate the chlorine by nitrate of silver, and determine its amount, either by collecting and weighing the precipitate, or by the volumetric method with chromate of potassium (i. 266).

II. VOLUMETRIC METHODS. 1. By *neutralisation.* See ANALYSIS, VOLUMETRIC (i. 261).—If sulphuric acid is the standard acid used, and the number of burette divisions of the standard alkaline solution required to neutralise equal weights of the standard sulphuric acid and of the nitric acid to be tested, are denoted by $p$ and $p'$, then the quantity of nitric acid ($HNO^3$) contained in 100 parts by weight of the acid under examination is given by the formula

$$x = 100 \;.\; \frac{63}{49} \;.\; \frac{p}{p'} = 128{\cdot}57 \; \frac{p}{p'}$$

If for example $p = 22$ and $p' = 50$, then $x = 56{\cdot}5$, or 100 grammes of the acid contain 56·5 grammes of real nitric acid. The percentage of nitric anhydride will be found by substituting 54 for 63 in the preceding formula.

2. *By the oxidation of Ferrous salts* (Pelouze's process).—A ferrous salt heated with nitric acid is converted into a ferric salt, with evolution of nitric oxide, every 3 at. iron ($Ffe = 56$) thus further oxidised corresponding to 1 at. nitric acid decomposed:

$$6FfeO + 2HNO^3 = 3Ffe^2O^3 + 2NO + H^2O.$$

A quantity of pure iron (harpsichord wire), more than can be converted into ferric oxide by the nitric acid to be estimated, is dissolved in excess of hydrochloric acid, contained in a long-necked flask; a known weight of the nitric acid or nitrate to be tested is then added, and the whole boiled till the liquid acquires a clear yellow colour. It is then diluted with water, and the excess of iron still present as ferrous salt is estimated by means of a standard solution of permanganate of potassium, as described under ANALYSIS, VOLUMETRIC (i. 263).

This process is well adapted for analysing mixtures of sulphuric and nitric acids used in the manufacture of gun-cotton, for mixtures of nitric acid with water, and is much used for the valuation of saltpetre. To ensure accuracy, access of air to the flask must be carefully avoided, as the nitric oxide which is generated would be thereby converted into a higher oxide of nitrogen, and thus peroxidise a further portion of the iron. Other sources of error are the reduction of a portion of the permanganic acid by nitric oxide remaining in the liquid, and the escape of nitric acid without having acted on the iron solution. To obviate these sources of inaccuracy, Fresenius (Ann. Ch. Pharm. cvi. 217) recommends the following method of operating. A long-necked tubulated retort, having a capacity of about 200 cubic centimetres, being placed with its neck inclined slightly upwards, about 1·5 grammes of pure iron wire is introduced into the bulb, and from 30 to 40 cubic centimetres of pure fuming hydrochloric acid is poured in. A stream of hydrogen gas, previously washed with potash-ley, is then passed into the retort by a glass tube passing through the tubulure, and entering the retort to the depth of about half-an-inch, and the neck of the retort is connected with a U-tube containing a small quantity of water. The bulb of the retort is sunk in a water-bath, and heated gently till the iron is completely dissolved. The solution is left to cool in the current of hydrogen; the current is then strengthened, and a quantity of the nitrate to be tested (not exceeding 0·4 gramme for saltpetre) having been weighed out in a small test-tube, is introduced, together with the tube, through the neck of the retort into the bulb. The connection of the neck of the retort with the U-tube is then restored; the contents are heated in the water-bath for a quarter of an hour; the retort is then removed from the water-bath, and heated over a lamp to brisk ebullition, till the solution, which is at first dark-coloured from absorption of nitric oxide gas, has acquired the light brown colour of ferric chloride, after which the boiling is continued for a few minutes longer. Care must be taken not to allow any portion of the salt to dry on the sides of the retort. Before the boiling is arrested, the stream of hydrogen must be accelerated, to prevent air from entering through the U-tube as the boiling ceases. The solution, after cooling in the current of hydrogen, is largely diluted with water, and the quantity of iron still remaining as ferrous salt is determined by means of permanganate or chromate of potassium.

A modification of this process proposed by C. D. Braun (J. pr. Chem. lxxxi. 421)

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consists in boiling the nitrate with an acid solution of ferrous chloride, in an atmosphere of carbonic anhydride, till all the nitric oxide is drawn off, then warming the solution with iodide of potassium, whereby iodine is separated, according to the equation—

$$\mathrm{FfeCl^3 + KI = FfeCl^2 + KCl + I},$$

and estimating the liberated iodine by means of sulphurous acid or hyposulphite of sodium.

*Schlösing's method.*—This method, also founded on the reducing action of boiling hydrochloric acid and ferrous chloride on nitrates, consists in collecting the nitric oxide evolved in the reaction over milk of lime, to free it from any hydrochloric acid that may pass over with it, carefully preserving it from contact of air, then transferring it into another vessel, and converting it into nitric acid by mixing it with oxygen in a vessel containing water; the quantity of this acid is then determined volumetrically by means of a standard solution of lime in sugar-water. This method has the advantage of not being affected by the presence of organic matter —which would vitiate the result obtained by Pelouze's process, by reducing a portion of the permanganic acid used to oxidise the ferrous salt and making the amount of nitric acid come out too small. It has been applied by Schlösing to the determination of nitric acid in tobacco; but it is difficult of execution, and not generally applicable. (Chem. Gaz. 1854, p. 398.)

3. *By the reducing action of Mercury* (Crum, Ann. Ch. Pharm. lxii. 233).—This method resembles the last, inasmuch as it depends on the collection of the nitric oxide evolved in the reaction, but differs from it, in completing the determination by the direct measurement of this gas, instead of by its reconversion into nitric acid. A weighed quantity of the nitrate is introduced into a graduated glass tube filled with mercury, and standing over mercury; a quantity of water sufficient to dissolve the salt is then passed up, and lastly a large excess of strong sulphuric acid. The nitric acid thus set free is reduced by the mercury to nitric oxide, which collects at the top of the vessel, the decomposition, accelerated by occasional agitation, being complete in about two hours. The level of the sulphuric acid is then read off, and a warm concentrated solution of ferrous sulphate is passed up to the top of the liquid. This absorbs the whole of the nitric oxide, leaving only a small quantity of nitrogen, arising from air left in the tube. The volume of gas absorbed is then observed, and the amount of nitric acid in the salt thence determined by calculation. This method, which gives exact results, has been applied by Crum to the determination of nitric acid, not only in saltpetre, but also in gun-cotton, after it had been ascertained that the presence of organic matter did not interfere with the liberation of the nitric oxide. To introduce the gun-cotton, and likewise pulverulent substances, above the mercury, Crum encloses them in a small glass tube. H. Rose recommends wrapping them in filtering paper.

4. *By the reducing action of copper at a red heat.*—When the vapours evolved by igniting a nitrate are passed over red-hot metallic copper, the copper takes up the whole of the oxygen and liberates the nitrogen, which may be collected and measured over mercury. The apparatus used and the mode of operating are the same as in Dumas' method for the absolute determination of nitrogen in organic bodies (see ANALYSIS, ORGANIC, i. 242). 1 part by weight of nitrogen corresponds to 3·857 parts $\mathrm{NO^5}$.

If the nitrate contains water, a chloride of calcium tube must be inserted between the combustion-tube and the gas-delivery tube, in order to absorb the water, and determine its amount by weight.

5. *By conversion into Ammonia.*—Nitric acid, as already observed (p. 84), is converted, by the action of nascent hydrogen evolved by the action of zinc on dilute acids or on solution of potash, into ammonia, each molecule of ammonia produced corresponding to 1 molecule of nitric acid:

$$\mathrm{HNO^3 + H^8 = NH^3 + 3H^2O}.$$

The reaction may be applied in various ways to the estimation of nitric acid.

*a. Martin's method.*—The salt or solution containing the nitric acid (after being boiled with excess of potash, to expel any ammonia that may be present), is treated with washed metallic zinc and sulphuric or hydrochloric acid; and, after the reaction is finished, the liquid is distilled with potash, to expel the ammonia, which is either estimated volumetrically by means of a standard acid liquid, or received in a bulb-apparatus containing hydrochloric acid, and subsequently precipitated by platinic chloride. A considerable quantity of zinc must be used, equal to at least four times the weight of the nitric acid to be estimated, because a portion of the hydrogen always escapes in the free state without acting on the nitric acid. The reaction is not interfered with by the presence of nitrogenous organic bodies, such as uric acid, quinine, the organic matters in mineral waters, &c.; gelatin retards it, but does not interfere with the final result.

*b. Harcourt's method* (Chem. Soc. J. xv. 383).—In this process, the hydrogen is evolved by the action of caustic potash solution on zinc in contact with iron (p. 157). A standard solution of sulphuric acid is used for the collection and determination of the ammonia, the excess of acid employed being finally determined by means of a standard solution of caustic potash. Or the ammonia may be condensed in hydrochloric acid and precipitated by chloride of platinum; but the volumetric method gives perfectly exact results. The result is not affected by the presence of sulphate of potassium or chloride of sodium.

For the estimation of nitric acid in other than alkaline nitrates, it is sometimes advisable to separate the base before proceeding to determine the nitric acid as above. Nitrate of barium, when directly submitted to this method of analysis, gives perfectly good results; but nitrate of lead showed a slight deficiency in the amount of nitric acid, due probably to an action of dissolved oxide of lead on the surface of the zinc.

6. *By reduction to Nitric Oxide and subsequent conversion of that compound into Ammonia.*—The conversion of the nitric acid into nitric oxide is effected, as in Pelouze's method (p. 86), by boiling the solution of the nitrate with ferrous chloride and free hydrochloric acid; and the nitric oxide is converted into ammonia, either by passing it mixed with hydrogen over platinum-sponge heated nearly to redness:

$$\text{NO} + \text{H}^5 = \text{NH}^3 + \text{H}^2\text{O},$$

by which method, however, the conversion into ammonia is completely effected only when the quantity of nitric oxide present is very small, that is to say, when only a small quantity of nitrate is operated on; or, secondly, and more effectually, by passing the nitric oxide mixed with sulphydric acid gas, over nearly red-hot soda-lime:

$$2\text{NO} + 3\text{H}^2\text{S} + 2\text{CcaO} = 2\text{NH}^3 + \text{CcaSO}^4 + \text{CcaS}^2.$$

In either case, each molecule of ammonia produced corresponds to one molecule of nitric oxide, and therefore also (p. 87) to one molecule of nitric acid. The ammonia produced by the reaction is collected in an absorption-apparatus in a measured quantity of standard sulphuric acid, and the excess of acid used is determined by a standard alkaline solution. This process was devised especially for the estimation of small quantities of nitric acid existing in plants, soils, waters, &c. From 10 to 100 grammes of the substance (or of the residue obtained by evaporating the water) is exhausted with boiling water, and the concentrated solution is treated as above described. (G. Ville, Compt. rend. xi. 939 and 987.)

### *Metallic Nitrates.*

NITRATE OF ALUMINIUM.—The *normal salt*, $\text{All}'''\text{N}^3\text{O}^9.9\text{H}^2\text{O}$, crystallises from a concentrated solution of hydrate of aluminium in nitric acid, in oblique, rhombic, very short prisms, which melt at 73°, solidify to a crystalline mass on cooling, deliquesce in the air, and dissolve very easily in water and in nitric acid. Half an ounce of the pulverised crystals mixed with an equal weight of acid carbonate of sodium or ammonium, produced, on solution in water, a fall of temperature from +10·5° to −23·3° (Ordway, Ann. Ch. Pharm. lxxvi. 247; see also Salm-Horstmar, Jahresb. 1850, p. 301). This salt treated with hydrate of aluminium appears to yield a series of basic salts analogous to the basic ferric nitrates (p. 94) (Ordway). Berzelius obtained a basic nitrate of aluminium in the form of a pasty mass by precipitating the neutral salt with ammonia.

NITRATE OF AMMONIUM. $(\text{NH}^4)\text{NO}^3$. *Nitrum flammans.* (See AMMONIACAL SALTS, i. 192.)

NITRATE OF BARIUM. $\text{BaNO}^3$ or $\text{Bba}''\text{N}^2\text{O}^6$. *Baryta-saltpetre.*—Prepared by treating the solution of sulphide of barium or the native carbonate (*Witherite*) with dilute nitric acid, or by precipitating the solution of the sulphide or chloride with nitrate of sodium. It crystallises in regular octahedrons and combinations of that form with others of the regular system, especially the cube. The crystals are permanent in the air, white, transparent, or translucent, have a specific gravity of 3·1848 (Karsten), and a sharp, saline, bitter taste; decrepitate when heated, and melt at a comparatively low temperature. At a red heat the salt decomposes, giving off oxygen, nitrogen, and nitric peroxide, and leaving a residue of pure baryta. It detonates slightly with combustible bodies, and decomposes with a yellowish light when thrown on glowing coals. It dissolves in water with slight depression of temperature. 1 pt. of the salt dissolves in 20 pts. water at 0°; in 12·5 pts. at 15°; in 5·9 pts. at 45°; in 3·4 pts. at 86°; and in 2·8 pts. at 106° (Gay-Lussac). According to Karsten, it dissolves in 11·66 pts. water at 20°, forming a solution of specific gravity 1·0678. In water containing nitric acid it is much less soluble, so that a neutral solution from which nothing will crystallise yields an additional crop of crystals on addition of nitric acid: hence also the necessity of using dilute nitric acid in preparing the salt from the carbonate, &c. In strong nitric acid it is quite insoluble; also in alcohol.

From a solution cooled to between 12° and 0°, Hirzel (*Zeitschr. f. Pharm.* 1854, p. 49) once obtained a hydrated salt containing $Bba''N^2O^6.2H^2O$.

An *aceto-nitrate of barium*, $Bba''(NO^3)(C^2H^3O^2).4H^2O$, is obtained by dissolving acetate of barium in excess of the nitrate, and crystallises from the mother-liquor after the excess of nitrate has separated, in large, right, rhombic prisms. (Lucius, Ann. Ch. Pharm. ciii. 113.)

**Nitrates of Bismuth.** The *normal salt*, $Bi'''N^3O^9.5H^2O$ or $Bi^2O^3.3N^2O^5.10H^2O$, is obtained by dissolving the pulverised metal or the oxide or carbonate in moderately strong nitric acid. The concentrated solution, which corrodes paper, and must therefore be filtered through asbestos or pounded glass, deposits the salt on evaporation in large crystals, which are very deliquescent, extremely caustic, and melt in their water of crystallisation when gently heated.

*Basic salts.*—A bismuth-nitrate having the composition $2Bi'''NO^4.H^2O = \left.\begin{matrix}\overset{'''}{Bi^2}.H^2\\(NO^2)^2\end{matrix}\right\}O^6$ or $Bi^2O^3.N^2O^5.H^2O$, is obtained by heating the normal salt to 78° (Graham, Ann. Ch. Pharm. xxix. 16), to 150° Gladstone (Chem. Soc. Mem. iii. 480). According to Ruge (Jahresb. 1862, p. 163), the normal salt heated for a certain time to 78° leaves the basic salt $Bi'''NO^4.HNO^3 = \left.\begin{matrix}Bi'''H\\(NO^2)^2\end{matrix}\right\}O^3$ or $Bi^2O^3.2N^2O^5.H^2O$; but if it be kept at that temperature till it no longer loses weight, the residue consists of $2Bi'''NO^4.H^2O$.

The acid solution of the normal salt is decomposed by water, with precipitation of a white basic salt formerly called *magistery of bismuth*. The composition of this precipitate is variously stated by different chemists, and appears to vary according to the quantity of water added, and the length of time for which the washing is continued. According to Ruge (*loc. cit.*) it consists mainly of the salt $Bi'''NO^4.H^2O$ or $Bi^2O^3.N^2O^5.2H^2O$, mixed with variable quantities of $Bi^2O^3.2BiNO^4.H^2O$ or $2Bi^2O^3.N^2O^5.H^2O$, the proportion of the latter increasing with the quantity of wash-water used. (See also Handw. d. Chem. vii. 176.)

**Nitrate of Cæsium**, $CsNO^3$. See Cæsium (i. 1115).

**Nitrate of Cadmium.** $CdNO^3.2H^2O$ or $Ccd''N^2O^6.4H^2O$.—Tufts of needles and prisms which, according to Meissner, deliquesce in the air, dissolve in alcohol, but without colouring the flame. According to Ordway (Sill. Am. J. [2] xxvii. 14), the salt melts at 59·5°, boils at about 132°, and remains clear and mobile on prolonged boiling till $\frac{3}{4}$ths of the water has gone off.

**Nitrate of Calcium.** $CaNO^3.2H^2O$ or $Cca''N^2O^6.4H^2O$.—This salt occurs on many parts of the earth's surface where the conditions are favourable to the formation of nitric acid, and calcium-salts (especially the carbonate) are likewise present. In many limestone caverns, those of Kentucky for example, it takes the form of silky efflorescences of a white or grey colour. It also occurs on the floors and walls of stables and other badly-drained buildings in which urine, blood, and other animal matters are left to putrefy. From the soil it often passes into well-water. When it forms on walls it causes rapid disintegration of the mortar, because, being very soluble and deliquescent, it is rapidly carried away by rain-water and atmospheric moisture; hence it is called the saltpetre-rot. In France, Prussia, and other countries of Europe it is formed artificially in saltpetre-plantations, consisting of heaps of decomposing vegetable and animal matter mixed with cinders, chalk, marl, &c., which are frequently moistened with urine, dunghill-water, waste soap-suds, &c. After exposure to the air for two or three years, the mass is lixiviated, and the crude liquor, which is chiefly a solution of nitrate of calcium, mixed however with the nitrates and chlorides of potassium, sodium and magnesium, is treated with carbonate, sulphate or chloride of potassium, in order to convert the nitrate of calcium into nitrate of potassium (see *Richardson and Watts's Chemical Technology*, vol. i. pt. 4, pp. 281—289).

Pure nitrate of calcium is best prepared by neutralising nitric acid with lime or carbonate of calcium. The solution, when evaporated to dryness, leaves the anhydrous salt, which has a specific gravity of 2·472 (Kremers), a warm bitter taste, dissolves easily in water and in alcohol, and may be heated to incipient fusion without decomposition. The partially decomposed salt is phosphorescent (*Baldwin's phosphorus*). At a higher temperature it is decomposed, giving off oxygen and nitric peroxide. It detonates slightly with combustible bodies.

A very strong aqueous solution of the salt crystallises with difficulty in deliquescent six-sided prisms terminated by acute pyramids—monoclinic combinations, according to Marignac—containing $Cca''N^2O^6.4H^2O$; according to Mitscherlich, the same hydrate

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is precipitated as a crystalline powder from the aqueous solution on addition of nitric acid. According to **Ordway** (*loc. cit.*) the hydrated salt melts at 44°, but if heated somewhat above its melting point, remains liquid till it has cooled down to the ordinary temperature, and if then touched with a crystal of the same salt, solidifies quickly, with considerable rise of temperature and contraction. Its specific gravity at 15·5°, is 1·90 in the solid, and 1·70 in the liquid state. The fused salt begins to boil at 132°, and remains clear during boiling down, till about one-third of the water has gone off, and then deposits the anhydrous salt, without loss of acid. The anhydrous salt evolves great heat on combining with water.

**NITRATES OF CERIUM.**—*a. Cerous nitrate*, $\mathrm{CeNO^3.2H^2O}$ or $\mathrm{Cce''N^2O^6.4H^2O}$, is obtained by dissolving ceroso-ceric oxide in nitric acid in presence of alcohol or some other reducing substance. The filtrate evaporated to a syrup yields the salt on cooling, as a faint rose-coloured crystalline mass, which gives off half its water at 150° and decomposes at 200°. (**L. J. Lange**, J. pr. Chem. lxxxii. 129.).

*Ammonio-cerous nitrate*, $\mathrm{(NH^4)NO^3.Cce''N^2O^6.8H^2O}$, obtained by evaporating a mixture of equal parts of the moderately concentrated solutions of the component salts, and crystallising over lime and chloride of calcium, is colourless, very soluble in water and alcohol, and deliquesces in moist air. (**Holzmann**, J. pr. Chem. lxxxiv. 76.)

A mixture of cerous nitrate and nitrate of potassium concentrated to a syrup and then left over oil of vitriol, yields small crystals of *potassio-cerous nitrate*, which gave in one analysis results agreeing with the formula $\mathrm{4KNO^3.3Cce''N^2O^6.4H^2O}$, but were not found to be of constant composition (**Lange**).—*Magnesio-cerous nitrate*, $\mathrm{Mmg''N^2O^6.Cce''N^2O^6.8H^2O}$, is obtained on adding alcohol to the mixed solutions of its component salts, in faint rose-coloured crystals, soluble in water and in alcohol; they give off 3 at. water at 110°, and the rest at 200°, melting at the same time (**Lange**). According to **Holzmann**, this salt is colourless and contains only 6 at. water. The double salts of cerous nitrate with the nitrates of *manganese*, *cobalt*, *nickel*, and *zinc*, are similar in composition (with 8 at. water) to the magnesium salt, and crystallise very easily from solutions made as nearly neutral as possible, in regular six-sided tables; they sometimes, however, exhibit hemihedral forms, and frequently have three alternate sides longer than the intermediate ones. The manganese salt gives off 4 at. water at 150°. (**Lange.**)

*Ceric oxide* dissolves slowly in nitric acid, forming a reddish-yellow liquid, which leaves on evaporation a reddish-yellow viscous mass, exhibiting distinct indications of crystallisation. It absorbs water from the air, and leaves when ignited a ceroso-ceric oxide which, according to Marignac, has nearly the composition $\mathrm{3Cce''O.2}\overset{'''}{\mathrm{Cce}}{}^2\mathrm{O^3}$.

An *ammonio-ceroso-ceric nitrate*, $\left.\begin{matrix}\mathrm{(NH^4)^4}\\ \mathrm{Cce''}\end{matrix}\right\}\mathrm{N^6O^{18}.}\overset{'''}{\mathrm{Cce}}{}^2\mathrm{N^6O^{18}.3H^2O}$, is obtained by mixing the solutions of nitrate of ammonium and ceroso-ceric nitrate and evaporating over lime and chloride of calcium; it forms nodular groups of very deliquescent, orange-red crystals, consisting of microscopic six-sided prisms. (**Holzmann**, *loc. cit.*)

**NITRATES OF CHROMIUM.** *Normal chromic nitrate*, $\mathrm{Ccr^2O^3.3N^2O^5.18H^2O}$ or $\mathrm{Ccr'''N^3O^9.9H^2O}$, is obtained by dissolving chromic hydrate in nitric acid. The solution, which is blue by reflected, red by transmitted light, dries up when evaporated to a gummy fissured mass, which is dark green both by transmitted and by reflected light, and after being heated over the water-bath for several hours, dissolves only partially in water, forming a brown solution (**Hayes**). According to **Ordway** (Sill. Am. J. [2] ix. 30; xxvii. 14) the normal salt crystallises, though with difficulty, from warm water, in purple oblique rhombic prisms containing 9 at. water, which melt at 37° to a green liquid, boiling at 125·5°, and form with cold water a purple solution which turns green when heated.

*Basic Salts.*—Normal chromic nitrate dissolves chromic hydrate, the solution remaining clear till it contains $\mathrm{8Ccr^2O^3}$ to $\mathrm{3N^2O^5}$; by careful addition of alkali, two-thirds of the acid may be withdrawn without producing permanent turbidity. The crystallised normal salt, heated over the water-bath till the loss of weight amounts to 39 per cent., leaves a dark green viscid residue, very soluble in water, and consisting of $\mathrm{Ccr^2O^3.2N^2O^5.12H^2O}$; on continuing the heat, more acid and water escape, and the spongy residue which then remains dissolves quickly in water, forming a dark brown solution containing chromate and nitrate of chromium (**Ordway**, Sill. Am. J. [2] xxvi. 197). According to **Siewert** (Ann. Ch. Pharm. cxxvi. 86), the saturated solution of chromic oxide in cold nitric acid contains the salt $\mathrm{Ccr^2O^3.2N^2O^5}$; and the hot saturated solution contains the salt $\mathrm{2Ccr^2O^3.3N^2O^5}$. From the latter, ether-alcohol precipitates chromic hydrate, while blue normal chromic nitrate remains in solution.

**NITRATE OF COBALT**, $\mathrm{CoNO^3.3H^2O}$ or $\mathrm{Cco''N^2O^6.6H^2O}$ (or $\mathrm{5H^2O}$ according to **Millon**) forms red prismatic crystals of specific gravity 1·83, according to **Bödeker**, which melt below 100°, and give off water at higher temperatures, the colour of the liquid changing from violet-red to green, and finally swell up, give off red nitrous vapours, and leave black cobaltoso-cobaltic oxide. The aqueous solution has a crimson colour, and may be used as a sympathetic ink. It is also much used as a reagent in blow-pipe experiments (i. 213).

A *basic salt*, $6CcoO.N^2O^5.5H^2O$ or $Cco^3N^2O^8.3CcoH^2O^2.2H^2O$, is formed as a blue precipitate, when a de-aërated solution of the normal salt is treated with excess of ammonia out of contact of air. After washing and drying, it forms a green powder, probably containing cobaltoso-cobaltic hydrate. (Winkelblach.)

The nitrates of the *cobalt-ammoniums* have been already described (i. 1052–1055).

Nitrates of Copper. *Normal cupric nitrate*, $CuNO^3$ or $Ccu''N^2O^6$, is obtained by dissolving metallic copper, cupric oxide, or cupric carbonate in dilute nitric acid. The solution is green at first (perhaps from admixture of cupric nitrite, and becomes blue only after standing for some time. From the blue solution at temperatures not below 20° (26° according to Ordway), the salt is deposited in dark blue prismatic crystals, containing $Ccu''N^2O^6.3H^2O$, according to Graham, Gladstone, and Ordway; $4H^2O$, according to Garhardt. This hydrate melts at 114·5°, and boils at 170°, giving off nitric acid, and leaving a green basic salt (Ordway). At lower temperatures, pale blue prisms are deposited containing 6 at. water: they effloresce in vacuo over oil of vitriol, giving off half their water, melt at 18° (at 26·4° according to Ordway), and are resolved into a liquid and crystals of the tri-hydrated salt. The latter decomposes at 65° into free acid and a basic salt (Graham):

$$3(CcuN^2O^6.3H^2O) \;=\; Ccu^3N^2O^8 \;+\; 4HNO^3 \;+\; 7H^2O.$$

A *basic cupric nitrate*, $3Ccu''O.N^2O^5.H^2O \;=\; \overset{''}{C}cu^3N^2O^8.H^2O$ (Graham), $4Ccu''O.N^2O^5.3H^2O \;=\; Ccu''O.\overset{''}{C}cu^2N^2O^8.3H^2O$ (Garhardt), is formed by gently heating the normal salt (to 66°—300°), or by boiling its solution with copper or cupric hydrate, or mixing it with a small quantity of alkali; also by treating cupric oxide with strong nitric acid, even in excess. It is a green powder, insoluble in water, soluble in acids; it bears the temperature of melting lead almost without decomposition, but is decomposed at a red heat, leaving cupric oxide; it also yields cupric oxide when boiled with potash (Proust). According to Vogal and Reischauer (Jahresb. 1859, p. 216), the salt $4Ccu''O.N^2O^5.3H^2O$ is obtained in light, iridescent, greenish-blue laminæ, by boiling the mixed solutions of normal cupric nitrate and nitrite of potassium, or the green liquid obtained by passing nitrous acid gas into water in which cupric hydrate is suspended.

*Di-ammonio-cupric nitrate*, $Ccu''(NH^4)^2N^4O^{12}$, crystallises very easily from aqueous solution, and explodes violently when the solution is evaporated by heat beyond a certain degree of concentration.

*Nitrate of Ammo-cuprammonium*, $Ccu''N^2O^6.4NH^3$, has been already partially described (ii. 81). According to Marignac (Compt. rend. xlv. 650), it forms rhombic crystals with the predominating faces $\infty P$, $\infty\breve{P}\infty$, $\breve{P}\infty$, and angles $\infty P : \infty P = 122° \, 35'$; $\breve{P}\infty : \breve{P}\infty$ over the principal axis $= 115° \, 10'$; twins often occur with composition face $\infty\breve{P}\infty$.

Nitrate of Didymium, $DiNO^3$ or $Ddi''N^2O^6$.—Easily soluble in water: the solution is rose-red when dilute, with a violet tinge when concentrated: a syrupy solution solidifies on cooling to a deliquescent mass of the hydrated salt, which melts and gives off its water when heated above 300°. The anhydrous salt dissolves easily in alcohol of 96 per cent., and a mixture of alcohol and ether, but is insoluble in pure ether. When strongly heated it gives off nitrous vapours, and ultimately leaves a residue of brown peroxide of didymium. If the decomposition be stopped at a certain point, and the residue treated with water, there remains a white mass, apparently consisting of a basic salt, $\overset{''}{D}di^2N^2O^8.Ddi''H^2O^2.4H^2O$. (Marignac, Ann. Ch. Phys. [3] xxxviii. 148; see also Hermann, Rép. Chim. pure, 1861, p. 53.)

Nitrate of Erbium. Permanent in the air; mostly colourless, sometimes slightly reddish; forms a colourless solution.

Nitrate of Glucinum, $2GNO^3.3H^2O$ or $Gg''N^2O^6.3H^2O$.—Obtained by decomposing the sulphate with nitrate of barium, as a difficultly crystallisable, very deliquescent salt, which melts at 60°, and boils at 140·5°, remaining clear when boiled down till the thermometer rises to 160°, and fluid till cooled to 16°; the fused mass solidifies rapidly on addition of strong nitric acid. When heated for twenty hours in a steam-bath, it left a thick transparent residue, amounting to 60 per cent. of its weight, perfectly soluble in water, and consisting of $Gg''N^2O^6.Gg''H^2O^2.2H^2O$. This basic salt also remains dissolved when the aqueous solution of the normal salt is treated in the cold with excess of carbonate of glucinum, whereas, on boiling, the whole of the glucina is precipitated in the form of a more highly basic salt. By the action of hydrate of glucinum, the normal nitrate may be converted into the tribasic nitrate, $Gg''^{3}N^{2}O^{8}$. (**Ordway**, Sill. Am. J. [2] xxvi. 197; xxvii. 14.)

**NITRATE OF GOLD?** Fine gold-leaf, and gold recently precipitated by ferrous sulphate, dissolves in fuming nitric acid; but the solution is very unstable, being decomposed even by agitation with water, with precipitation of auric oxide, or if nitrous acid is present, of metallic gold. Auric oxide and hydrate likewise dissolve in fuming nitric acid, forming a similar solution.

**NITRATES OF IRIDAMMONIUMS** (see IRIDIUM-BASES, AMMONIACAL, iii. 324).

**NITRATES OF IRON.** *a. Ferric Nitrates.*—The *normal salt*, $Fe^{2}O^{3}.3N^{2}O^{5}.18H^{2}O$ or $Ffe'''N^{3}O^{9}.9H^{2}O$, is prepared by dissolving metallic iron in nitric acid of specific gravity 1·29, till the liquid has taken up about 10 per cent. of the metal, and then adding an equal volume of nitric acid of specific gravity 1·43. The solution, on cooling, deposits the salt in oblique rhombic prisms of specific gravity 1·6835 at 20°, colourless or with a faint lavender-blue tint, slightly deliquescent, very soluble, with a yellow-brown colour, in water, very slightly soluble in cold nitric acid. At 47·2° they melt to a deep red liquid, which remains liquid till cooled to 20°, and has then a specific gravity of 1·6712; part of the acid goes off at 100°; the liquid boils at 125°, and complete decomposition takes place at a red heat (**Ordway**, *loc. cit.*). **Hausmann** (Ann. Ch. Pharm. lxxxix. 109), by evaporating the red-brown solution of iron in nitric acid to a syrup, at a gentle heat, then adding half the volume of nitric acid, and leaving the solution to crystallise, obtained prismatic crystals containing $Ffe''N^{3}O^{9}.6H^{2}O$, and melting at 35°. R. **Wildenstein** (J. pr. Chem. lxxxiv. 243) obtained the same hydrate in limpid cubic crystals, from a large quantity of *iron mordant* containing a very small quantity of free acid (prepared by saturating slightly diluted nitric acid with iron, and evaporating to 48° or 50° Baumé).

*Basic Salts.*—**Ordway** has obtained basic ferric nitrates containing from 2, 3, 6, 8, 12 to 24 molecules of ferric oxide to 3 at. nitric anhydride, namely by mixing the solution of the normal salt with recently precipitated ferric hydrate in various proportions; they are all soluble in water, and the solutions when evaporated yield red mostly deliquescent powders. The solutions have a deep red colour, are not decomposed by boiling or dilution, but when saturated with ferric oxide, they yield a precipitate of that oxide on addition of chloride of sodium, sulphate of potassium, chloride of ammonium, sulphate of sodium, cupric sulphate, &c., but are not precipitated by neutral acetate of lead, cupric acetate, or alcohol. **Scheurer-Kestner** (Compt. rend. xlvii. 927) has obtained the two salts $2Ffe^{2}O^{3}.N^{2}O^{5}.HO$ and $Ffe^{2}O^{3}.N^{2}O^{5}$. These, as well as the normal salt, are decomposed by water, the normal salt yielding $2Ffe^{2}O^{3}.N^{2}O^{5}.8H^{2}O$, the first of the two basic salts just mentioned yielding $3Ffe^{2}O^{3}.N^{2}O^{5}.2H^{2}O$, and the second $4Ffe^{2}O^{3}.N^{2}O^{5}.3H^{2}O$. **Hausmann**, by evaporating the solution of iron in nitric acid to a syrup, adding half the volume of strong nitric acid, and leaving the solution to crystallise, obtained colourless prisms containing $Ffe^{2}O^{3}.3N^{2}O^{5}.12H^{2}O$. By mixing a very concentrated solution of this salt with water till the colour became reddish-yellow, then boiling, and adding nitric acid after cooling, an ochre-coloured precipitate was formed, containing $8Ffe^{2}O^{3}.2N^{2}O^{5}.3H^{2}O$. By adding a very large quantity of water to a highly concentrated and slightly acid solution of the nitrate, an ochre-coloured precipitate was sometimes formed, containing $36Ffe^{2}O^{3}.N^{2}O^{5}.48H^{2}O$. By treating iron excess with nitric acid, a precipitate was obtained having the composition $8Ffe^{2}O^{3}.N^{2}O^{5}.12H^{2}O$.

*β. Ferric Aceto-nitrates* (**Scheurer-Kestner**, Ann. Ch. Phys. [3] lxiii. 422; Rép. Chim. pure, iv. 95).—These, and similar salts containing chlorine and other monatomic radicles are obtained:—1. By leaving mixtures of ferric hydrate and monatomic acids (nitric, hydrochloric, acetic, &c.) to act upon one another for several days at 40°.—2. By mixing a monatomic acid with a very concentrated solution of a ferrous salt, or with the dry salt, and oxidising the mixture with nitric acid.—3. By the mutual action of the component salts, *e.g.* of ferric acetate and ferric nitrate.—4. By the action of an acid on a ferric salt containing another acid.

*Ferric Diaceto-nitrate*, $Ffe'''(C^{2}H^{3}O^{2})^{2}(NO^{3}).3H^{2}O$, crystallises in slender blood-red needles or right rhombic prisms of considerable size;—*ferric aceto-dinitrate*, $Ffe'''(C^{2}H^{3}O^{2})(NO^{3})^{2}.4H^{2}O$, in right rhombic prisms;—*ferric tetraceto-nitrate*, $\overset{vi}{F}fe^{2}(C^{2}H^{3}O^{2})^{4}(NO^{3})(HO).4H^{2}O$, in hard, shining, red-brown, right rhombic prisms;—*ferric triaceto-nitrate*, $\overset{vi}{F}fe^{2}(C^{2}H^{3}O^{2})^{3}(NO^{3})(HO)^{2}.2H^{2}O$, in oblique rhombic prisms, resembling ferricyanide of potassium.

γ. *Ferrous nitrate*, $Fe^2O.N^2O^5$ or $Ffe''N^2O^6$.—Prepared by precipitating ferrous sulphate with an equivalent quantity of nitrate of barium, and evaporating the filtrate in vacuo over oil of vitriol; or by adding sulphide of iron to cold dilute nitric acid, and evaporating the solution in vacuo. If the solution were evaporated by heat, ferric salts would be formed. The salt is likewise obtained by treating iron borings or filings with cold dilute nitric acid, nitrate of ammonium being formed at the same time, and no evolution of gas taking place:

$$10HNO^3 + Ffe^4 = 4Ffe''N^2O^6 + (NH^4)NO^3 + 3H^2O.$$

The solution thus obtained may be heated nearly to boiling without decomposition.

According to Scheurer-Kestner (Compt. rend. xlvii. 927), nitric acid of specific gravity 1·034 yields with iron nothing but ferrous nitrate and ammonia, whereas acid of specific gravity 1·073 yields the same products together with ferric nitrate; and acid of specific gravity 1·115 and upwards, only ferric nitrate, and no ammonia. In the latter case, the solution contains basic salts, as well as the normal salt, and in greater proportion as the acid was more concentrated.

Ferrous nitrate crystallises from solution after some time in four-sided bevelled prisms, having a very faint greenish colour and sharp taste, deliquescent and very soluble in water.

The solution of iron filings in cold dilute nitric acid is used in dyeing.

**NITRATE OF LANTHANUM**, $LaNO^3.\frac{3}{2}H^2O$ or $Lla''N^2O^6.3H^2O$, separates from a syrupy solution in large prismatic crystals which deliquesce in the air and dissolve easily in water and in alcohol. If the water be very carefully drawn off from the crystals, the residual anhydrous salt may be fused without decomposition, but if the temperature be then raised above the melting-point, a small quantity of nitric acid goes off, and the residual basic salt solidifies on cooling to a kind of enamel which almost immediately afterwards crumbles to a bulky white powder, and with such force that the particles are scattered to a considerable distance. At a red heat the salt is completely decomposed, leaving a residue of oxide (Mosander). The hydrated salt melts at about 40° and boils at about 120°. (Ordway.)

**NITRATES OF LEAD.** The *normal salt*, $Pb^2O.N^2O^5$ or $Ppb''N^2O^6$, is obtained by dissolving litharge or metallic lead at the boiling heat, in slightly diluted nitric acid, which should be free from hydrochloric and sulphuric acids. The neutral nitrate crystallises in large octahedrons, with the secondary faces of the cube, sometimes transparent, although generally white and opaque; specific gravity 4·509 (Schröder); 4·235 (Buignet). The crystals are anhydrous; they are soluble in 7½ times their weight of cold, and in a much smaller quantity of hot water. (Mitscherlich.)

According to Kremers (Pogg. Ann. xcii. 499) 1 pt. of the nitrate of lead dissolves in 2·58 pts. water at 0°; in 2·07 pts. at 10°; in 1·65 pts. at 25°; in 1·25 pts. at 45°; in 0·99 pts. at 65°; in 0·83 pts. at 85°; and in 0·72 pts. at 100°. The saturated solution boils at 103·5°. The specific gravities at 17·5° of solutions of various strengths are as follows (Kremers, Pogg. Ann. ciii. 57; civ. 133):

| Weight of salt in 100 pts. water. | Specific gravity of solution. | Weight of salt in 100 pts. water. | Specific gravity of solution. |
|---|---|---|---|
| 34·79 | 1·3816 | 11·60 | 1·1022 |
| 23·30 | 1·2274 | 7·73 | 1·0661 |
| 15·46 | 1·1415 | | |

See also Schiff (Ann. Ch. Pharm. cx. 75). Nitrate of lead is insoluble in *alcohol*, and in strong *nitric acid*, which indeed precipitates it from aqueous solution; soluble in saturated solutions of *nitrate of potassium* and *nitrate of barium*. (For full details respecting its solubility in water and other solvents, see *Storer's Dictionary of Solubilities*, p. 382.)

Nitrate of lead is decomposed at an incipient red heat, yielding a mixture of oxygen gas and nitric peroxide (p. 76), and leaving the yellow protoxide of lead (iii. 549).

*Basic salts.*—The *diplumbic salt*, $2Ppb''O.N^2O^5 = Ppb''O.Ppb''N^2O^6$ (Berzelius) or $2Ppb''O.N^2O^5.H^2O = Ppb''HNO^4$ (Pelouze), is produced by boiling the normal salt with white lead and water (Pelouze), or 1 pt. of the normal salt with 1 pt. lead oxide and water (Chevreul), or by treating the solution of the normal salt with a quantity of ammonium not sufficient to throw down all the lead as oxide. It crystallises from the hot aqueous solution in white grains or nacreous laminæ and needles having a sweet astringent taste. It is but slightly soluble in cold, more soluble in hot water; according to Pohl, 1 pt. of it dissolves in 5·15 pts. water at 19·2°.

*Triplumbic nitrate*, $3Ppb''O.N^2O^5$ or $P\overset{''}{pb}{}^3N^2O^6$, is precipitated with ½ at. water

($2P\overset{''}{p}b^3N^2O^8.3H^2O$), on treating the solution of the normal salt with a slight excess of ammonia, as a white powder, slightly soluble in pure water and precipitated by addition of many salts which do not decompose it. The same salt is precipitated, according to A. Vogel, jun., with twice the preceding quantity of water ($P\overset{''}{p}b^3N^2O^8.3H^2O$), on adding nitrate of potassium or sodium to a solution of basic acetate of lead. It is sparingly soluble in boiling water, crystallises on cooling in nodules of needle-shaped crystals, and gives off its water of crystallisation in vacuo at 205°.

*Hexplumbic nitrate*, $6Ppb''O.N^2O^5.H^2O = P\overset{''}{p}b^3N^2O^8.3Ppb''O.H^2O$, is obtained by precipitating the normal salt with excess of ammonia, and digesting the washed precipitate with ammonia. It is a white powder, nearly insoluble in water.

*Formo-nitrate of Lead*, $\left.\begin{matrix}P\overset{''}{p}b^2 \\ NO^2 \\ (CHO)^3\end{matrix}\right\}O^4.H^2O$, obtained by dissolving formate of lead in a hot nearly saturated solution of the nitrate, crystallises by slow cooling in large rhombic plates, permanent in the air, and sparingly soluble in water.

*Phospho-nitrate of Lead*, $\left.\begin{matrix}P\overset{''}{p}b^2 \\ NO^2 \\ (PO)'''\end{matrix}\right\}O^4.H^2O$ or $Ppb''N^2O^6.P\overset{''}{p}b^3P^2O^8.2H^2O$, is obtained by adding a soluble phosphate to excess of nitrate of lead, as a crystalline precipitate, insoluble in water, soluble in nitric acid, and crystallises in six-sided plates derived from an oblique rhombic prism. It is decomposed by boiling water into nitrate and orthophosphate of lead, and when heated to redness leaves a residue of basic phosphate, $Ppb''O.P\overset{''}{p}b^3P^2O^8$. (Gerhardt, Ann. Ch. Pharm. lxviii. 286.)

**Nitrate of Lithium**, $LiNO^3$.—The anhydrous salt crystallises at 15° in rhombic prisms, like nitrate of potassium; of specific gravity 2·334, according to Kremers (Pogg. Ann. xcii. 520); according to Troost (Ann. Ch. Phys. [3] li. 134), in rhombohedral crystals, R . oR, having the angle of the terminal edges = 105° 40′; specific gravity 2·442. Below 10° the hydrate, $2LiNO^3.5H^2O$, crystallises in thin deliquescent prisms (Troost). The salt dissolves easily in water and in alcohol; the solutions taste like saltpetre, but very pungent. The specific gravities of solutions containing various proportions of the anhydrous salt, according to the determinations of Kremers (Pogg. Ann. cxiv. 41), are exhibited in the following table:—

| $LiNO^3$ in 100 pts. | Specific gravity at 19·5°. | $LiNO^3$ in 100 pts. | Specific gravity at 19·5°. |
|---|---|---|---|
| 14·2 | 1·0769 | 57·5 | 1·2550 |
| 26·7 | 1·1346 | 77·4 | 1·3154 |
| 40·6 | 1·1930 | | |

Nitrate of lithium easily forms super-saturated solutions, which solidify at 1°, often in masses of slender needles, the temperature of the solution rising to 27°. (Kremers.)

**Nitrate of Magnesium**, $MgNO^3.3H^2O$ or $Mmg''N^2O^6.6H^2O$.—This salt occurs in the mother-liquor of the saltpetre-plantations, and was detected by Berzelius in the well-waters of Stockholm. It is prepared by dissolving *Magnesia alba* in nitric acid, and crystallises from the concentrated solution in deliquescent rhombic prisms and needles (monoclinic according to Marignac), soluble in $\frac{1}{2}$ pt. cold water and in 9 pts. alcohol of specific gravity 0·840, less soluble in absolute alcohol. When dried over oil of vitriol, they give off 4 at. water. They melt when heated, and at the temperature of melting lead give off, according to Graham and Chodnew, 5 at. water, leaving the monohydrated salt, $Mmg''N^2O^6.H^2O$, which, at a still higher temperature, gives off the rest of the water and part of the nitric acid, leaving the *trimagnesic salt*, $M\overset{''}{m}g^3N^2O^8$. Einbrodt, on the other hand, doubts the existence of the monohydrated salt, inasmuch as he finds that the hex-hydrated salt begins to give off nitric acid before it has parted with the fifth molecule of water.

Nitrate of magnesium forms an *alcoholate*, $Mmg''N^2O^6.6C^2H^6O$ (see i. 80).

**Nitrate of Manganese**, $MnNO^3.3H^2O$ or $Mmn''N^2O^6.6H^2O$.—White longitudinally-striated needles, deliquescent, and soluble in alcohol.

**Nitrates of Mercury.**—*a. Mercuric nitrates.*—When mercuric oxide is dissolved in excess of nitric acid, and the solution is evaporated at a gentle heat, the *normal salt*, $HgNO^3H^2O$ or $Hhg''N^2O^6.2H^2O$, is left in the form of a syrupy liquid, which retains its constitution unaltered for several months. By further evaporation over oil of vitriol, it yields bulky deliquescent crystals, consisting of the hydrate, $2Hhg''N^2O^6.H^2O$, which easily give up a portion of their acid (*Handw. d. Chem.* vii. 165). According to C. G. Mitscherlich (*Gmelin's Handbook*, vi. 74), the crystals obtained by evaporating the acid solution of the normal salt consist of the basic

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salt $\text{Ħg}''O.\text{Ħg}''N^2O^6.2H^2O$. A concentrated solution made as neutral as possible yields, when cooled to 15°, large colourless rhombic plates with angles of about 67°, melting at 6·6°, and having the composition $\text{Ħg}''N^2O^6.8H^2O$. (Ditten, Jahresb. 1854, p. 366.)

*Basic salts.*—The clear liquid obtained by fusing the crystals of the octohydrate just mentioned deposits the salt $\text{Ħg}''O.\text{Ħg}''N^2O^6.3H^2O$, in short colourless needles, which become opaque when exposed to the air and white by contact with water. Both this salt and the normal salt are decomposed by water, the *trimercuric salt*, $3\text{Ħg}''O.N^2O^5.H^2O$ or $\overset{\prime\prime}{\text{Ħg}}{}^3N^2O^8.H^2O$, being first separated as a white pulverulent mass, and afterwards gradually converted into red mercuric oxide. The trimercuric salt with 1 at. water is likewise produced by heating either of the preceding salts till it is converted into a pulverulent mass, then pulverising it, and treating it seven or eight times with cold water. It begins to give off water at about 120° C., and nitrous fumes at 250°. A *hexmercuric nitrate*, $6\text{Ħg}''O.N^2O^5$ or $3\text{Ħg}''O.\overset{\prime\prime}{\text{Ħg}}{}^3N^2O^8$, is obtained, according to Kane, as a brick-red powder by boiling the trimercuric salt with water.

Normal mercuric nitrate treated with ammonia yields a number of nitrates of mercurammoniums, already described (iii. 917, 920).

*Double Salts of Mercuric Nitrate.* α. With *Mercuric Cyanide.*—$\text{Ħg}^2(NO^3)^2Cy^2.2H^2O$.—Produced, according to Desfosse, when a solution of mercuric nitrate is mixed with cyanide of potassium, and crystallises in white micaceous scales.

β. With *Mercuric Iodide.* $\text{Ħg}''N^2O^6.\text{Ħg}I^2$ (Louisville, Rigel); $2\text{Ħg}''N^2O^6.\text{Ħg}''I^2$ (Preuss).—Obtained by dissolving the iodide in a boiling solution of the nitrate; or by treating mercurous or mercuric iodide with nitric acid. White nacreous scales which are decomposed by water and by alcohol.

Another iodonitrate, $\text{Ħg}''N^2O^6.2\text{Ħg}''I^2$, is obtained, according to Liebig, in small red crystals on mixing a boiling solution of mercuric nitrate with half as much iodide of potassium as is required for the complete separation of mercuric iodide. The solution filtered from these crystals, mixed with a little nitric acid, and saturated while warm with mercuric iodide, yields after some days, white silky needles of the compound $2\text{Ħg}''N^2O^6.3\text{Ħg}''I^2$.

All these mercuric iodonitrates are decomposed by water, the iodide separating and the nitrate dissolving. When heated, they melt, give off nitrous acid and a sublimate of mercuric iodide, and leave mercuric oxide.

γ. With *Iodide of Silver*, $2.\text{Ħg}''N^2O^6.4AgI.H^2O$. Separates from a solution of silver-iodide in hot aqueous mercuric nitrate, in slender needles which are decomposed by water.

δ. With *Mercuric Phosphate.* This double salt is formed by mixing a solution of sodium-phosphate with excess of mercuric nitrate.

ε. With *Mercuric Phosphide*, $3(\text{Ħg}''N^2O^6.\text{Ħg}''O).\overset{\prime\prime}{\text{Ħg}}{}^3P^2$. Produced by passing phosphoretted hydrogen gas through a dilute acid solution of mercuric nitrate. After washing with water, it forms a yellow powder, which must be dried in a vacuum. It detonates with great violence when heated, less strongly by percussion; also in chlorine gas, probably in consequence of heat developed by the chemical action which ensues.

ζ. With *Mercuric Sulphate*, $\text{Ħg}''N^2O^6.2\text{Ħg}''S$. Sulphydric acid gas passed through a solution of mercuric nitrate in quantity not sufficient for complete decomposition produces a white precipitate which must be washed with water, and then dried; if the washing is continued beyond a certain time, the compound begins to decompose and turn yellowish. An excess of sulphydric acid converts it wholly into black mercuric sulphide. It is likewise decomposed and blackened by aqueous carbonate of potassium or sodium. Hot nitric acid decomposes it with formation of sulphuric acid. (H. Rose.)

*Mercurous Nitrates.* The *normal salt*, $\text{Ħg}NO^3.H^2O$, is formed by prolonged digestion of metallic mercury in excess with cold moderately strong nitric acid, and separates in colourless somewhat efflorescent, monoclinic crystals. According to Gerhardt and Marignac (Jahresb. 1849, p. 285), the same salt is formed when the liquid is moderately warmed; it is best however to decant the solution as soon as the first violent action has somewhat subsided, and leave the still acid liquid to crystallise by cooling. It sometimes, according to Gerhardt, deposits prismatic crystals of a basic salt, but these, if left in the liquid, are gradually converted into the normal salt. The latter is soluble without decomposition in a small quantity of water, but a larger quantity converts it into a basic salt. When heated with water it is resolved into pernitric oxide and mercuric oxide; $2\text{Ħg}NO^3 = \text{Ħg}''O + NO^2$.

*Basic salts.*—The above-mentioned prismatic crystals which sometimes separate, according to Gerhardt, from the solution of excess of mercury in warm dilute nitric acid, are most readily obtained, according to Marignac, when the crystals of the normal salt are warmed in their mother-liquor, in contact with excess of mercury, and the solution is then left to crystallise by cooling. (The following basic salt is often formed at the same time.) The crystals are colourless, shining, non-efflorescent prisms, belonging to the trimetric system. Gerhardt and Marignac obtained the same results by the analysis of these crystals; nevertheless they are regarded by Gerhardt as $\mathrm{Hhg^2O.4HhgNO^3.H^2O}$, and by Marignac as $\mathrm{Hhg^2O.6HhgNO^3.H^2O}$.

Another basic mercurous nitrate, $\mathrm{Hhg^2O.2HhgNO^3.H^2O}$,—according to Gerhardt, $\mathrm{Hhg^2O.3HhgNO^3.H^2O}$,—is obtained when the salt produced by the action of nitric peroxide vapour on mercury is triturated with a small quantity of water, and the mixture then heated to boiling; also when normal mercurous nitrate is suspended in water and the water heated to boiling; also, according to Marignac, when the solution or mother-liquor of either of the preceding salts is boiled for several hours with excess of mercury, the water being replaced as it evaporates; or when the crystals of either of the preceding salts are left to stand for several hours in contact with their mother-liquor and excess of mercury. The crystals are triclinic, permanent in the air, colourless, hard and shining. (Gerhardt, Jahresb. 1847—48, p. 447.—Marignac, *loc. cit.*)

Lefort, by prolonged digestion of mercury in excess with dilute nitric acid at 40°—50°, or by evaporating the product of the action of strong nitric acid on excess of mercury to dryness, and treating the residue with boiling water, obtained a salt which formed large prismatic crystals, perhaps identical with those obtained as above by Gerhardt and Marignac. Lefort, however, regards them as $\mathrm{Hhg^2O.2HhgNO^3.2H^2O}$.

By the action of cold water on the preceding salts, Gerhardt and Marignac obtained a light yellow powder consisting of $\mathrm{Hhg^2O.4HhgNO^3.3H^2O}$, as previously established by Kane. Gerhardt regards it as the above-mentioned triclinic salt in the amorphous state.

Mitscherlich has described another salt, $\mathrm{Hhg^2O.4HhgNO^3.3H^2O}$, which is perhaps identical with the salt $\mathrm{Hhg^2O.4HhgNO^3.H^2O}$, obtained by Gerhardt (*vid. sup.*). Mitscherlich obtained it by leaving cold dilute nitric acid in contact with excess of mercury, till the crystals of the normal salt which form at first, dissolve and are replaced by others. Crystals of different form, but of the same composition (therefore dimorphous), are formed, according to Mitscherlich, when the normal mercurous salt is warmed with mercurous oxide and water containing a little nitric acid. In this way, large limpid crystals are obtained which dissolve in a small quantity of water, but are decomposed by a large quantity, either cold or hot.

The solution of mercurous nitrate is precipitated by ammonia, yielding a black precipitate of very variable composition, constituting the so-called *Mercurius solubilis Hahnemanni* (iii. 920).

Mercurous nitrate forms double salts with the nitrates of barium, strontium and lead.

The *lead-salt*, $\mathrm{2Ppb''N^2O^6.(Hhg^2O.2HhgNO^3)}$ or $\left.\begin{matrix}\mathrm{Ppb''^2}\\ \mathrm{Hhg^4}\end{matrix}\right\}\begin{matrix}\mathrm{(NO^3)^6}\\ \mathrm{O}\end{matrix}$, is obtained, according to Städeler, on mixing a moderately concentrated solution of mercurous nitrate with nitrate of lead, as a white heavy precipitate consisting of microscopic octahedrons with cubic modification: dilute solutions yield it in larger crystals having an adamantine lustre. It dissolves without alteration in boiling nitric acid, but is decomposed by pure water. The *barium-* and *strontium-salts* are similar in form and composition.

*Mercuroso-mercuric nitrate*, $\mathrm{Hhg^2O.2Hhg''O.N^2O^5}$ or $\left.\begin{matrix}\mathrm{NO^2}\\ \mathrm{Hhg'}\\ \mathrm{Hhg''}\end{matrix}\right\}\mathrm{O^2}$, is formed by the gradual oxidation of mercurous nitrate; also when 1 pt. of mercury is boiled with 1½ pt. nitric acid of specific gravity 1·2 till completely dissolved (Wittstock). According to Gerhardt (Jahresber. 1849, p. 285), the light yellow salt which covers the hotter parts of the sides of the vessel in which mercurous nitrate is evaporated, consists of this mercuroso-mercuric salt; the same chemist obtained it, with evolution of nitric oxide, by fusing normal mercurous nitrate.

Nitrates of Molybdenum.—*Molybdic nitrate* is obtained in solution by saturating nitric acid with molybdic hydrate, or by digesting metallic molybdenum in dilute nitric acid. It cannot be obtained in the solid state, as the solution when concentrated beyond a certain point, gives off nitric oxide and leaves molybdic acid.

*Molybdous nitrate* is obtained by dissolving molybdous hydrate in dilute nitric acid; if the hydrate is in excess, a basic salt is formed. The solutions are very unstable and quickly decompose, depositing molybdic acid. (Berzelius.)

*Permolybdic nitrate* or *nitrate of molybdic acid* is obtained by dissolving molybdic anhydride in nitric acid (iii. 1037).

Nitrate of Nickel. $\mathrm{NiNO^3.3H^2O}$ or $\mathrm{Ni''N^2O^6.6H^2O}$.—Emerald-green, eight-sided prisms,—monoclinic, according to Marignac,—which effloresce in dry and deliquesce in moist air, dissolving in 2 pts. of cold water, also in alcohol, and when heated leave a yellowish-green pulverulent basic salt, then peroxide, and finally protoxide of nickel.

An *ammoniacal nitrate of nickel*, $Nni''N^2O^6.4NH^3.H^2O$ (or $2H^2O$ according to Laurent) $= \left.\begin{matrix}Nni''\\H^{14}\\(NO^2)^2\end{matrix}\right\}\begin{matrix}N^4\\O^3\end{matrix}$, is deposited in octahedral crystals, from a warm concentrated solution of nickel in ammonia. The crystals when exposed to the air, give off ammonia and crumble to a bluish-white powder.—This salt unites with chloride of nickel-ammonium, forming rather large azure-blue octahedrons of the double-salt, $\left.\begin{matrix}Nni''\\H^{14}\\(NO^2)^2\end{matrix}\right\}\begin{matrix}N^4\\O^3\end{matrix}.NH^4NiCl.3H^2O$.

**Nitrate of Osmium.** $Os''N^2O^6$.—Osmious hydrate dissolves with green colour in cold nitric acid, and the saturated solution dries up on evaporation to a green transparent varnish. (Berzelius.)

**Nitrate of Palladium.** $Pd''N^2O^6$.—Cold nitric acid slowly dissolves palladium, without evolution of nitric oxide, the liquid becoming charged with nitrous acid; if the liquid is warmed, solution takes place more quickly, with evolution of nitric oxide. The brown solution evaporated to a syrup, and then left over oil of vitriol, deposits long narrow rhombic prisms, of brown-yellow colour, and very deliquescent. From a dilute solution, the whole of the palladium is gradually deposited in the form of a basic salt. By evaporation between 100° and 120° also, the normal salt is almost wholly converted into a basic salt. If the solution is evaporated at a low temperature, and the residual salt treated with water, a turbid solution is obtained, and a basic salt remains behind, which according to Fischer, is completely converted into oxide by heating to 120°—130°. For the basic salt precipitated from the solution of the normal salt by water or by a small quantity of potash, Kane gives the formula $4Pd''O.N^2O^5.4H^2O$.

The nitrates of the palladammoniums will be described under PALLADIUM-BASES, AMMONIACAL.

**Nitrates of Platinum.** ***Platinic Nitrate***, $Pt''N^2O^6$ or $Ppt^{iv}N^4O^{12}$, is obtained by dissolving platinic hydrate in nitric acid, or better by decomposing the sulphate with nitrate of barium, or by mixing the chloride with nitrate of potassium as long as a precipitate is thereby produced, a third of the platinum present being thereby converted into platinic nitrate. The decanted dark brown liquid yields by evaporation, a mass of the thickness of honey, which after evaporation to dryness, dissolves only partially in water, leaving a basic salt.

For the nitrates of the platinammoniums, see PLATINUM-BASES, AMMONIACAL.

*Potassio-platinic nitrate.*—When caustic potash is added to a solution of platinic nitrate, only half the base separates as hydrate, the rest as a basic double salt of much lighter colour than the hydrate. *Sodio-platinic nitrate* is known only in solution. It is formed by decomposing sodio-platinic chloride with hydrate of sodium, at a heat below redness, washing out the resulting chloride of sodium with water, and dissolving the residual sodio-platinic oxide in nitric acid. The dark yellow solution yields, with nitrate of silver, a yellow precipitate soluble in nitric acid. (Döbereiner.)

***Platinous nitrate.***—Platinous hydrate dissolves in dilute colourless nitric acid, and the green-brown solution dries up to a viscid, greenish, dark brown mass, in which platinic oxide is gradually formed at the expense of the nitric acid, and more abundantly as the acid is in greater excess. (Berzelius.)

**Nitrate of Potassium.** $KNO^3$. *Saltpetre, Nitre, Prismatic Saltpetre, Potash-nitre, Nitrum fixum.*—This salt is very widely diffused as a natural product, occurring constantly, though in small proportion only, as a constituent of vegetable soil, and according to Boussingault (Compt. rend. xliv. 108–119) of spring and river water. It is never found in large beds like nitrate of sodium; but veins of it occur in the sandstone of Bradford County, Pennsylvania (Ellet, Edinb. Phil. J. lvii. 367). The chalk and other recent calcareous formations are particularly rich in saltpetre. On the banks of the Seine, near Roche-Guyon and Mousseau, there are several caves which are used as stables; in the front part of these caves, looking towards the south, the saltpetre accumulates, especially during the summer season, and in such quantity that it is collected several times in a year, and continually reproduced. Lavoisier found in the earth taken from the cave of Fouquières, $3\frac{1}{3}$ per cent., and in that of Mousseau, $5\frac{2}{3}$ per cent. nitrate of potassium, after the aqueous extract of the earth had been treated with potash to convert the nitrates of calcium and magnesium into nitrate of potassium.

The saltpetre caverns of Ceylon, which are natural caves in a dolomitic rock containing felspar, are of especial importance. Some of these caves, like that of Boullatwellegode, are the resort of large flocks of bats, whose excrement collects in them: in others, as in that of Memoora, there are none of these animals. Davy found, in a specimen of rock from this cave, 2·4 per cent. nitrate of potassium, 0·7 nitrate of magnesium, 0·2 sulphate of magnesium, 26·5 carbonate of calcium, 0·4 water, and 60·8 of residue insoluble in dilute nitric acid, and consisting of quartz, mica and talc. Similar caves are found to exist on the coast of the Adriatic, in Italy (Palo di Mofetta), in Tennessee, Kentucky, on the Missouri and Crooked Rivers in North America, in Africa, and in Teneriffe.

In South America, and in some districts of India, Arabia, Persia, Spain, and Hungary, the mode of occurrence of saltpetre is somewhat different. In these districts, nitrates are found widely disseminated through the soil, but never extending to any great depth below the surface, not lower, indeed, than the air can easily penetrate. The infiltration of rain and dew dissolves these salts, and the solution rising to the surface by capillary action, is evaporated by the action of the sun and air, and forms an efflorescence on the surface. In Bengalese saltpetre earth, from the district of Tirhût, Davy found 8·3 per cent. nitrate of potassium, 3·7 nitrate of calcium, 0·8 sulphate of calcium, 0·2 chloride of sodium, 35·0 carbonate of calcium with traces of magnesium, 12·0 water with a little organic matter, and 40·0 matter insoluble in nitric acid. The soil in some parts of Spain is also impregnated with saltpetre, as in New Castile, Arragon, Catalonia, La Mancha, Granada, &c.

The formation of nitric acid in these several localities is in all probability due to the oxidation of ammonia (p. 83); for the production of saltpetre is always found to take place most abundantly where there is a large quantity of vegetable or animal matter in a state of putrefaction, or where the air contains a considerable quantity of ammonia resulting from such decomposition. Hence it is that the quantity of saltpetre naturally produced in tropical climates very far exceeds that which is formed in Europe, the luxuriant vegetation of the tropics supplying a never-failing source of ammonia, while the high temperature and the moisture of the air facilitate its oxidation. An indispensable condition, however, for the formation of nitrates in large quantity, is the presence of alkaline or earthy bases to fix the nitric acid as soon as it is formed: in the absence of such bases indeed, and under the reducing influence of organic matter, nitric acid already formed may be reconverted into ammonia: hence the non-production of nitrates in dung-heaps, where earthy matters are not present.

This theory is quite in accordance with the conditions which are found essential to the artificial production of saltpetre in temperate climates, as in the saltpetre plantations already described (p. 83), these conditions being an abundant supply of ammonia, the presence of earthy and alkaline bases, free access of air, and a mean temperature not lower than 15°—20°.

The solution obtained by lixiviating the *saltpetre-earth* thus formed consists, as already observed, chiefly of the nitrates of calcium and magnesium, with smaller quantities of the nitrates of potassium and sodium, besides alkaline chlorides. It is treated with carbonate of potassium (potashes) to convert the earthy nitrates into nitrate of potassium, which is deposited in an impure state from the filtered solution by crystallisation.

Natural saltpetre-earth is treated in a similar manner with wood-ashes, when the earthy nitrates predominate in it; that of Bengal however, which is rich in nitrate of potassium, does not require this treatment, the saltpetre being extracted from it merely by lixiviation, boiling and crystallisation.

The crude saltpetre thus obtained is contaminated with the chlorides of potassium and sodium (sometimes to the amount of 25 per cent.) besides organic (so-called extractive) matter. To remove these impurities, which are exceedingly objectionable in all the applications of saltpetre, whether for the preparation of nitric acid or the manufacture of gunpowder, the crude saltpetre is subjected to a refining process.

The greater part of the chloride of sodium, which always constitutes the greater part of the impurities present, and is much less soluble in boiling water than nitrate of potassium, is separated by treating the crude saltpetre with a quantity of boiling water sufficient to dissolve the whole of the nitrate of potassium, but not the whole of the chloride of sodium. Thus, suppose 6,000 lbs. of the crude salt containing 6 per cent. chloride of calcium and 14 per cent. chloride of sodium to be treated with 12,000 lbs. of boiling water; the solution will then takeplace in the following manner:

| | lbs. | The 12,000 lbs. of water are capable of dissolving at 100°: lbs. |
|---|---|---|
| Chloride of potassium | 360 | 684 |
| Chloride of sodium | 840 | 324 |
| Nitrate of potassium | 4800 | 4800 |
| | 6000 | |

There will then remain, when the water has ceased to act, 840 − 324 = 516 lbs. of chloride of sodium undissolved. This residual salt is scooped out of the pan, and the solution, after being diluted to a certain extent, is boiled with glue, to coagulate the extractive matters and cause them to rise as a scum to the surface. This having been removed, the concentrated solution is transferred to the crystallising pan, in which it is left to cool, and as soon as crystallisation begins, the liquid is constantly stirred, so as to prevent the formation of large crystals (which would inclose considerable quantities of mother-liquor in their cavities) and cause the nitrate of potassium to separate out in the form of a crystalline powder called *saltpetre-flour*. By this means, a mass of minute crystals of nitrate of potassium is obtained, merely contaminated with adhering mother-liquor, which is easily removed, partly by draining, and finally by washing with a saturated solution of pure nitrate of potassium, which, though unable to take up any more of that salt, is still capable of dissolving the alkaline chlorides contained in the adhering mother-liquor. It then only remains to dry the purified saltpetre by heat.

*Production of Nitrate of Potassium from Chile Saltpetre.*—Nitrate of sodium is easily converted into nitrate of potassium by adding it to a hot concentrated solution of carbonate of potassium. An immediate precipitation of carbonate of sodium takes place, and if this be removed as long as it continues to separate on further evaporation, and the remaining solution left to cool in the crystallising pans, *saltpetre-flour* is obtained, which merely requires washing and drying as above described to render it pure. 100 lbs. of nitrate of sodium require, according to the purity of the salt, from 80 to 100 lbs. of carbonate of potassium.

This mode of preparation is much easier than those already described, and in localities where potash is not too expensive, is now extensively adopted. The chief difficulty experienced in carrying it out arises from the presence of common salt in Chile saltpetre: for if more potash be added than is required to decompose the nitrate of sodium, the excess decomposes chloride of sodium to no purpose; and in the contrary case, the product is likely to be contaminated with undecomposed nitrate of sodium. The best way of averting this inconvenience is to purify the nitrate of sodium by previous crystallisation.

Some manufacturers render the potash caustic by means of lime before mixing it with the nitrate of sodium, and after keeping the mixed solution in a state of ebullition for some time, leave it to cool slowly in a closed vessel. Nitrate of potassium then crystallises out, and caustic soda remains in solution.

In Belgium, large quantities of saltpetre are obtained by decomposing nitrate of sodium with potash obtained from the ashes of the beet-root sugar manufacture. The nitrate of potassium from this source is very pure, and is produced at a very low price.

Nitrate of sodium may also be converted into nitrate of potassium by double decomposition with chloride of potassium in equivalent proportions (74·7 pts. KCl to 85 pts. of $NaNO^3$). On evaporating the mixed solution, chloride of sodium separates out first, while nitrate of potassium remains in the mother-liquor, and crystallises on cooling.

*Properties.*—Nitrate of potassium is dimorphous. It usually crystallises from concentrated aqueous solution in long six-sided prisms belonging to the trimetric system, and frequently exhibiting the combination $\infty P . \infty\bar{P}\infty . 2\breve{P}\infty . \breve{P}\infty . P$ (fig. 268, CRYSTALLOGRAPHY, ii. 147), or the same without $\breve{P}\infty$; also without P. The combinations $P . 2\breve{P}\infty . \infty P . \infty\breve{P}\infty$, and $P . 2\breve{P}\infty$ likewise occur. Ratio of axes $a : b : c = 0·589 : 1 : 0·701$. P : P in the brachydiagonal principal section = 131° 27′; (macr.) = 91° 29′; (basal) = 108° 12′; $\infty P : \infty P = 61° 0′$; $\breve{P}\infty : \breve{P}\infty$ (basal) = 70° 4′; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) = 109. Cleavage imperfect parallel to $\infty P$; somewhat easier parallel to $\breve{P}\infty$. Specific gravity, = 2·11 (Kopp); 2·1006 (Karsten); 2·100 (Schiff); 2·086 (Schröder). The crystals are anhydrous, but often contain mother-liquor inclosed in their cavities. Nitrate of potassium also crystallises in rhombohedral forms resembling ordinary calcspar. Frankenheim (Pogg. Ann. xcii. 354) observed that when a drop of saltpetre solution is left to evaporate under the microscope, rhombohedral crystals make their appearance, together with the ordinary prismatic crystals; if the evaporation takes place very slowly, the crystals are almost wholly rhombohedral, and these if touched with a prismatic crystal, immediately become turbid and are converted into a mass of prismatic crystals. On the other hand a prismatic crystal of saltpetre may be converted into a mass of rhombohedral crystals by heating it nearly to its melting point. All these phenomena may be very distinctly observed by means of the polarising microscope.

Nitrate of potassium is white, inodorous, and has a cooling bitter taste. When perfectly pure it dissolves, according to Gay-Lussac, in $7\frac{1}{2}$ pts. water at 0°, in nearly $3\frac{1}{2}$ pts. at 18°, in $1\frac{1}{3}$ pt. at 45°, in less than $\frac{1}{2}$ pt. at 90°, and in 0·4 pt. at 100°. According to H. Schiff (Ann. Ch. Pharm. cvii. 293) the specific gravities of aqueous solutions of nitrate of potassium of various strengths are as follows:

| Weight of $KNO^3$ in 100 pts. of solution. | Specific gravity of solution at 21°. | Weight of $KNO^3$ in 100 pts. of solution. | Specific gravity of solution at 21°. |
|---|---|---|---|
| 24·93 | 1·1683 | 8·31 | 1·0510 |
| 16·62 | 1·1073 | 5·54 | 1·0337 |
| 11·08 | 1·0695 | 2·77 | 1·0170 |

According to **Kremers** (Jahresb. 1861, p. 61), the specific gravity at 19·5° of solution of saltpetre containing 12·7 per cent. of saltpetre, is 1·0695; of a 23·7 per cent. solution, 1·1275. It is sparingly soluble in aqueous alcohol, quite insoluble in absolute alcohol.—**Schiff** (*ibid.* p. 87) has made the following determinations of the solubility of nitrate of potassium in spirits of wine of various strengths:

| Weight of anhydrous alcohol in 100 pts. of spirit. | Weight of $KNO^3$ in 100 pts. of solution saturated at 15°. | Weight of anhydrous alcohol in 100 pts. of spirit. | Weight of $KNO^3$ in 100 pts. of solution saturated at 15°. |
|---|---|---|---|
| 0 | 20·5 | 40 | 4·3 |
| 10 | 13·2 | 50 | 2·8 |
| 20 | 8·5 | 60 | 1·7 |
| 30 | 5·6 | 80 | 0·4 |

(See further, *Storer's Dictionary of Solubilities*, p. 389.)

Nitrate of potassium melts below a red heat without loss to a colourless liquid, which solidifies on cooling to a white opaque fibrous mass called in commerce *Mineral crystal, Nitrum tabulatum, Salprunellæ*: the commercial product often however contains nitrite of potassium, in consequence of too much heat having been employed in the fusion. At a red heat, saltpetre gives off oxygen gas, at first tolerably pure, but afterwards contaminated with a continually increasing quantity of nitrogen, and is thereby converted first into nitrite, then into a mixture of protoxide and peroxide of potassium. Saltpetre deflagrates in the fire with charcoal and other combustible bodies; as sulphur, phosphorus, iron, zinc, &c.; and even oxidises gold, silver, and platinum. By ignition in contact with copper foil, it is converted into nearly pure protoxide of potassium, which when dissolved in water, yields caustic potash. Iron, at a red heat, decomposes the saltpetre quite as easily as copper, but the product is contaminated with the foreign substances present in the iron. (**Wöhler**, Ann. Ch. Pharm. lxxxvii. 373.)

On the oxidising power of saltpetre at a red heat depends its use in the manufacture of gunpowder (ii. 956), and other explosive mixtures. It is frequently also employed in the preparation of *lucifer matches* instead of chlorate of potassium, and has the advantage of producing a composition which ignites by friction without the inconvenient and dangerous projection of burning particles, which often takes place on the ignition of ordinary matches made with the chlorate.

*Valuation of Saltpetre.*—For the various applications of saltpetre, and especially for the manufacture of gunpowder, it is important to possess a ready method of ascertaining its relative purity. One of the oldest methods is that of **Schwarz**, adopted in Sweden, which is based upon the appearance of the fractured surface of the melted salt, that of pure nitrate of potassium being coarsely radiate, whereas when chloride of sodium is present, this structure becomes less distinct, and with 3½ per cent. of that salt, is visible at the edges only, the interior of the mass being amorphous. This crude method is called the *refraction of saltpetre*, a term which has been somewhat strangely extended to other methods of valuation. In France **Riffault's** method is sometimes used, which consists in washing a weighed quantity of the saltpetre with a saturated solution of pure nitrate of potassium at 16°; this solution extracts the chlorides, leaving the pure nitrate, which is drained from mother-liquor on slabs of gypsum, then dried and weighed. This method, like the preceding, can give only rough approximations.

A more exact method is that of **Gay-Lussac**, which consists in igniting 1 pt. of the saltpetre with ½ pt. charcoal and 4 pts. common salt to moderate the action. The nitrate is thereby converted into carbonate, the amount of which can be estimated by titration with standard sulphuric acid. Errors may however arise in this process, partly from a portion of the nitrate remaining undecomposed, partly from formation of cyanide of potassium; but according to **Abel** and **Bloxam** (Chem. Soc. Qu. J. ix. 97), exact results may be obtained by the use of very finely divided carbon, namely **Brodie's** prepared graphite (i. 758), the proportions being 20 pts. saltpetre, 5 graphite, and 80 chloride of sodium. If the saltpetre contains sulphates, which will be reduced to sulphides by ignition with carbon, a small quantity of chlorate of potassium must be sprinkled on the surface of the mass immediately after removal from the fire; the sulphides will be thereby completely reconverted into sulphates.

The quantity of nitrate of potassium in a sample of commercial saltpetre may also be estimated by **Pelouze's** method, depending on the oxidation of ferrous chloride by nitric acid (p. 87), or by igniting the saltpetre with silica or anhydrous borax (p. 86).

In Austria, saltpetre is assayed by the method of **Husz**, founded on the varying solubility of nitrate of potassium in water at different temperatures. 5 oz. of the saltpetre to be tested are dissolved in 12 oz. of water at 50° C., and the temperature is observed at which the liquid just begins to deposit crystals. The percentage of nitrate of potassium is then determined by the following table, the results not being affected by the presence of chlorides.

*Crystallising points of solutions of Nitrate of Potassium of various degrees of concentration.*

| Temperature. Reaumur. | Quantity of pure saltpetre in 100 parts of the solution. | Quantity of pure saltpetre in 100 parts of the sample. | Temperature. Reaumur. | Quantity of pure saltpetre in 100 parts of the solution. | Quantity of pure saltpetre in 100 parts of the sample. |
|---|---|---|---|---|---|
| + 8° | 22·72 | 55 7 | + 14·25° | 30·00 | 75 |
| 8·25 | 22·53 | 56·3 | 14·50 | 30·36 | 75·9 |
| 8·50 | 22·80 | 57·0 | 14·75 | 30·72 | 76·8 |
| 8·75 | 23·08 | 57·7 | 15 | 31·09 | 77·7 |
| 9 | 23·36 | 58·4 | 15·25 | 31·46 | 78·6 |
| 9·25 | 23·64 | 59·1 | 15·50 | 31·83 | 79·6 |
| 9·50 | 23·92 | 59·8 | 15·75 | 32·21 | 80·5 |
| 9·75 | 24·21 | 60·5 | 16 | 32·59 | 81·5 |
| 10 | 24·51 | 61·3 | 16·25 | 33·97 | 82·4 |
| 10·25 | 24·81 | 62 | 16·50 | 33·36 | 83·4 |
| 10·50 | 25·12 | 62·8 | 16·75 | 33·75 | 84·4 |
| 10·75 | 25·41 | 63·5 | 17 | 34·15 | 85·4 |
| 11 | 25·71 | 64·3 | 17·25 | 34·55 | 86 4 |
| 11·25 | 26 02 | 65 | 17·50 | 34·90 | 87 4 |
| 11·50 | 26·32 | 65·8 | 17·75 | 35·38 | 88·4 |
| 11·75 | 26·64 | 66·6 | 18 | 35·81 | 89·5 |
| 12 | 26·96 | 67·4 | 18·25 | 36·25 | 90·6 |
| 12·25 | 27·28 | 68·2 | 18·50 | 36·70 | 91·7 |
| 12·50 | 27·61 | 69 | 18·75 | 37·15 | 92·9 |
| 12·75 | 27·94 | 69·8 | 19 | 37·61 | 94 |
| 13 | 28·27 | 70·7 | 19·25 | 38·01 | 95·2 |
| 13·25 | 28·61 | 71·5 | 19·50 | 38·55 | 96·4 |
| 13·50 | 28·95 | 72·4 | 19·75 | 39·03 | 97·6 |
| 13·75 | 29·30 | 73·2 | 20 | 39·51 | 98·8 |
| 14 | 29·65 | 74·1 | 20·25 | 40 | 100 |

According to **F. Toel** (Ann. Ch. Pharm. c. 78) Husz's method gives exact results only when 40 pts. of the saltpetre to be tested are dissolved in exactly 100 pts. of water at 45° R. (56¼ C. or 133¼ F.), the solution subsequently cooled by immersing the vessel in cold water, and the temperature at which crystallisation begins, carefully observed, the solution being constantly stirred as it cools. To ensure the right proportion, the saltpetre is dissolved in the proper quantity of water contained in a tared beaker glass with a thermometer inserted, and heated to 45°—50° R. in a water-bath, the water which evaporates while the salt is dissolving being replaced. The solution is filtered to remove any solid particles suspended in it, which might cause the crystallisation to take place too soon, and the first half which runs through is used for observing the temperature at which crystallisation begins. With 10 drachms of saltpetre and 25 drachms of water, the quantity of water which evaporates during the operation generally amounts to 8 or 10 grains, and that which is lost during the cooling and stirring to 2 or 3 grains.

By this method, Toel and Hoyermann also determine the amount of nitrate of sodium in nitrate of potassium, an impurity which generally exists in the salt prepared from Chile saltpetre, in consequence of imperfect decomposition. The amount of nitrate of potassium is first determined in the given sample, exactly in the manner just described; then about 7½ drachms are dissolved in 25 drachms of water, a drachm of carbonate of potassium is added, the crystallising point is observed, and the solution is boiled for an hour to convert the nitrate of sodium completely into nitrate of potassium. The solution is now left to cool to 50° R., the water being replaced as it evaporates, then filtered, and the crystallising point again observed. If the sample contained nitrate of sodium, the crystallising temperature will now be found higher than before, viz. 0·15° R. for 1 per cent. of nitrate of sodium, 0·35° R. for 2 per cent., 0·8° R. for 3 per cent. and 1·55° R. for 4 per cent.

The amount of nitrate of sodium in saltpetre may also be approximately determined by ascertaining the quantity of water which it absorbs when exposed to an atmosphere saturated with moisture. According to the observations made by the Prussian officers of artillery, it appears that pure nitrate of potassium exposed over the surface of water for fourteen days, remains comparatively dry, whilst nitrate of sodium placed under the same circumstances, absorbs 25 per cent. of water. When artificial mixtures of the two salts in a pure state, are subjected to the same treatment, the quantities of water absorbed are as follows:

| Mixture with percentage of nitrate of sodium | 0·5 | 1 | 3 | 5 | 10 | |
|---|---|---|---|---|---|---|
| Absorbed in 14 days . | 2·5 | 4 | 10 | 12 | 19 | Water, per cent. |

All gunpowder containing this variety of saltpetre would, of course, become moist in the same proportions, and would thus be rendered useless.

A third method of determination is based upon the alteration which an admixture of nitrate of sodium produces in the solidifying point of saltpetre heated above its melting point. Nitrate of potassium melts at 358° C. (674·4° F.), and nitrate of sodium at 313° C. (595·4° F.). For mixtures of 100 pts. nitrate of potassium with different proportions of nitrate of sodium, the following melting points have been observed.

| Quantities of $NaNO^3$ added to 100 pts. $KNO^3$. | Melting points. | Quantities of $NaNO^3$ added to 100 pts. $KNO^3$. | Melting points. |
|---|---|---|---|
| 10 pts. . | . 311° C. = 591·8°F. | 50 pts. . | . 229° C. = 444·2° F. |
| 20 „ . | . 280 = 586 | 60 „ . | . 244 = 471·2 |
| 30 „ . | . 250 = 482 | 70 „ . | . 262 = 503·6 |
| 40 „ . | . 230 = 446 | 80 „ . | . 281 = 537·8 |
| 45·7 „ . | . 226 = 438 | 90 „ . | . 298 = 568·4. |

The lowest melting-point is exhibited by a mixture of the two salts in equivalent proportions (45·7 per cent. of nitrate of sodium), which, according to Schaffgotsch, melts at 226° C., and according to Person at 219·8°.

Small quantities of nitrate of sodium mixed with nitrate of potassium may be detected by the yellow colour which sodium-compounds impart to the blowpipe flame, or still better by spectral analysis (iii. 622).

Small quantities of chlorides sometimes present in refined saltpetre are easily detected by nitrate of silver and estimated by means of a standard solution of that salt.

*Persoz's method for the complete analysis of Saltpetre* (Rép. Chim. app. 1861, pp. 253, 366).—The quantity of water is first determined by heating 50 grms. of the saltpetre in a platinum crucible, and weighing it after cooling, care being taken that the heat does not rise much above the melting point. If the saltpetre contains nitrate of calcium or magnesium, 1 grm. of dry chromate of potassium must be added, to prevent the decomposition of these salts.

To determine the insoluble matters, the fused mass is treated with water, the liquid filtered, and the undissolved matter washed, dried and weighed. The liquid is then concentrated to a determinate volume, N. The *chlorides* are estimated in this solution by means of two standard silver-solutions, one containing 27 grms., the other 2·7 grms. of silver in a litre. A cubic centimetre of the former corresponds to 0·01466 grm. of chloride of sodium, or to 0·01864 grm. of chloride of potassium.

The *sulphates* are likewise estimated volumetrically by means of a standard solution of chloride of barium, containing 259·8 grammes of this salt in a litre, and therefore corresponding to 0·179 gramme of sulphate of sodium or 0·208 gramme of sulphate of potassium. To make the determination, 200 cubic centimetres of the solution N, are mixed with a few drops of acid in a platinum dish, then heated to boiling, and the standard solution is cautiously added in slight excess. The saltpetre solution N is then gradually added from a burette to the liquid contained in the dish, till the excess of the baryta-solution is decomposed and the whole of the baryta precipitated. This last operation is rather tedious, because the liquid does not easily clarify, and it is necessary to filter a sample from time to time. From the proportion between the total volume of the liquid N used in the experiment, and the volume of baryta-solution present, the amount of sulphate in the saltpetre may be calculated. The *nitric acid* is estimated by igniting the fused saltpetre with acid chromate of potassium, the loss of weight giving the quantity of nitric anhydride; or the estimation may be made by any of the methods already given for the analysis of nitrates (pp. 85–89).

**Nitrate of Rhodium.** Sesquioxide of rhodium, or the corresponding hydrate, forms with nitric acid a dark red solution which yields a deliquescent salt of the same colour. *Sodio-rhodic nitrate*, $NaRh'''N^4O^{12}$, forms dark red crystals, easily soluble in water, insoluble in alcohol. (Berzelius.)

**Nitrate of Rubidium**, $RbNO^3$, crystallises in hexagonal combinations. $P \,.\, \infty P \,.\, P2 \,.\, \infty P2$, in which the length of the principal axis is 0·7079, and the angle P : P, in the terminal edges = 143° 0′, in the lateral edges = 78° 40′. It dissolves in 5 pts. water at 0°, and in 2·3 pts. at 10°. Behaves like saltpetre when heated. (Kirchoff and Bunsen, Phil. Mag. [4] xxii. 55.)

**Nitrate of Silver.** $AgNO^3$. *Lunar caustic. Lapis infernalis. Höllenstein.* —When a piece of pure silver is suspended in nitric acid, it dissolves for a time without effervescence at a low temperature, nitrous acid being produced, which colours the liquid blue; but if heat be applied or the temperature allowed to rise, the metal dissolves with violent effervescence, from the escape of nitric oxide. The nitrate of silver crystallises on cooling in colourless anhydrous crystals belonging to the trimetric system. Ratio of axes, $a : b : c = 0·9433 : 1 : 1·370$. P : P (brachyd.) = 104° 18′; (macr.) = 98° 51′; (basal) = 126° 48′; $\infty\breve{P}2 : \infty\breve{P}2$ (basal) = 55° 30′. Ordinary combination $P \,.\, oP \,.\, \infty\breve{P}2$; often with four P-faces lying in the same zone, so much developed that with the two basal faces oP, they give the crystal the aspect of a six-sided prism. Nitrate of silver is soluble in 1 part of cold, in ½ part of hot water, and in 4 parts of boiling alcohol. The solution does not redden litmus paper like most metallic salts, but is exactly neutral. Nitrate of silver melts at 219°, and forms a crystalline mass on cooling; it is cast into small cylinders for the use of surgeons. In this state it is sometimes adulterated with nitrate of potassium, which may be detected by the alkaline residue which the salt then leaves when heated before the blow-pipe—or with nitrate of lead, in which case the solution of the salt is precipitated by iodide of potassium, of a full yellow colour. When applied to the flesh of animals, it instantly destroys the organisation and vitality of the part. It forms insoluble compounds with many kinds of animal matter, and is employed to remove it from solution. When organic substances, to which a solution of nitrate of silver has been applied, are exposed to light, they become black from the reduction of the silver to the metallic state. A solution of nitrate of silver in ether is employed to dye the hair black. One part of nitrate of silver and 4 parts of gum arabic dissolved in 4 parts of water and blackened with a small quantity of Indian ink, form the indelible marking ink used for writing on linen (iii. 272).

*Ammonio-nitrates of Silver.*—A strong solution of silver-nitrate supersaturated with ammonia yields the compound $AgNO^3.2NH^3 = \left.\begin{matrix}Ag\\NO^2\\H^6\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}$ in shining rhombic crystals, exhibiting the combination $\infty P \,.\, \infty\breve{P}\infty \,.\, \breve{P}\infty$. It is very soluble in water, permanent at 100°, but decomposes at a higher temperature, giving off nitrogen and ammonia. Dry nitrate of silver absorbs ammonia-gas in such proportion as to form the compound $AgNO^3.3NH^3 = \left.\begin{matrix}Ag\\NO^2\\H^9\end{matrix}\right\}\begin{matrix}N^3\\O\end{matrix}$, which is a white coherent mass, soluble in water and giving off its ammonia when heated.

*Double Salts of Silver-nitrate.* α. With *Cupric Cyanide.*—Formed, according to Berzelius, when a solution of silver-nitrate is poured upon cupric cyanide recently precipitated from the nitrate. It is black, insoluble in water, and deflagrates with a green light.

β. With *Mercuric Cyanide.* $2AgNO^3.HhgCy^2.4H^2O$.—Crystallises from a warm mixed solution of the two salts, in large, limpid, nacreous prisms resembling saltpetre, sparingly soluble in cold, easily soluble in warm water and alcohol. (Wöhler.)

γ. With *Mercuric Nitrate.* $Hhg''N^2O^6.2AgNO^3$. Prisms soluble in water without decomposition. (Wöhler.)

δ. With *Bromide of Silver.* $AgNO^3.AgBr$.—Formed by melting the component salts together in atomic proportion. Solidifies into a crystalline mass at 182° (Schnauss. Kremers, Jahresb. 1855, p. 419). According to Riche (*ibid.* 1858, p. 207) and Risse (*ibid.* 1859, p. 229), it separates in silky needles from a solution of bromide of silver in a hot concentrated solution of the nitrate.

ε. With *Chloride of Silver.* Separates in slender prismatic needles from a solution of the chloride in a hot saturated solution of the nitrate. (Risse.)

ζ. With *Cyanide of Silver.* $AgNO^3.AgCy$.—When recently precipitated cyanide of silver is dissolved in a boiling concentrated solution of the nitrate, this double salt is deposited on slow cooling in slender needles having a strong lustre. It is decomposed by water, melts when heated, and then detonates with great force, leaving silver containing cyanogen.

*η*. With *Iodide of Silver.*—The compound $2AgNO^3.AgI$ separates in nacreous needle-shaped crystals from a solution of iodide of silver in a boiling concentrated solution of the nitrate (Weltzien, Ann. Ch. Pharm. xcv. 127). According to H. Risse (Jahresb. 1859, p. 228), it is best prepared by melting the component salts together in the required proportions, treating the resulting mass with a little boiling water, and leaving the oily body which settles to the bottom to crystallise on cooling. It blackens on exposure to light, melts at 105°, solidifies again at 98°, dissolves in a small quantity of water, but is decomposed by a larger quantity and by alcohol.

Another *iodonitrate*, $AgNO^3.AgI$, is obtained by heating a moderately strong acid solution of the nitrate with iodide of silver, and boiling the resulting mass for a long time with nitrate of silver and nitric acid. It then separates in needles which melt at 94° (Schnanss, Kremers, Jahresb. 1855, p. 429). According to Riche (*ibid.* 1858, p. 207), the product thus obtained is very unstable; and according to Risse (*loc. cit.*) it is merely a mixture of the preceding salt with iodide of silver.

*θ*. With *Nitrate of Sodium.*—A solution of nitrate of sodium mixed with excess of nitrate of silver deposits, first tabular crystals of silver-nitrate, and afterwards rhombohedral crystals, having the form of sodium-nitrate but containing the two salts in various proportions; from 2 to 4 at. $NaNO^3$ to 1 at. $AgNO^3$. (H. Rose, Pogg. Ann. cii. 436.)

NITRATE OF SODIUM. $NaNO^3$. *Cubic Saltpetre. Chile Saltpetre. Nitre.*—This salt occurs abundantly in South America as a natural mineral. In the district of Tarapaca, Northern Chile, the dry pampa for 40 leagues at a height of 3,300 feet above the sea, is covered with beds of it several feet thick, associated with gypsum, common salt, sulphate of sodium, and remains of ancient shells, indicating the former presence of the sea. The following are analyses of the crude nitre or *Caliche.*

| | Hayes. | Richardson and Browell. | | | |
|---|---|---|---|---|---|
| Nitrate of sodium . . . | 64·98 | 43·14 | 36·37 | 27·85 | 6·92 |
| Sulphate of sodium . . . | 3·00 | 26·30 | 11·67 | 43·20 | 0·68 |
| Sulphate of calcium . . . | . . | 1·36 | 1·36 | 0·68 | |
| Sulphate of magnesium . . | . . | trace | trace | 4·20 | |
| Chloride of sodium . . . | 28·69 | 11·40 | 44·80 | 18·30 | 88·70 |
| Iodide of sodium . . . | 0·63 | | | | |
| Insoluble matter . . . | 2·70 | 10·30 | 3·30 | 0·32 | 0·03 |
| Moisture . . . . | . . | 7·50 | 2·50 | 6·00 | 3·50 |
| | 100·00 | 100·00 | 100·00 | 100·55 | 99·83 |

A sample from Chile, analysed by Hochstetter, was found to contain 94·3 per cent. of nitrate of sodium, the remainder being composed of 2·0 chloride of sodium, 0·2 sulphate of potassium, 0·4 nitrate of potassium, 0·9 nitrate of magnesium, 2·0 water, and 0·2 insoluble matter.

The crude nitrate is refined by solution and crystallisation. The best refined nitre of commerce has been found to contain 97·70 per cent. nitrate of sodium, 1·84 chloride of sodium, 0·35 sulphate of sodium, and 0·11 water. The commercial salt frequently however contains not more than 90 to 92 per cent. nitrate of sodium; small quantities of iodide and iodate of sodium are of frequent occurrence in it, in addition to the foreign salts above mentioned. The great solubility of nitrate of sodium renders it difficult to purify from common salt; accordingly the commercial nitrate almost always contains about 2 per cent. of that impurity. The best mode of purifying it, on the small scale, is to heat the pulverised salt with nitric acid; the chlorides are thereby destroyed, and by solution and recrystallisation the nitrate is obtained perfectly pure.

Nitrate of sodium crystallises in obtuse rhombohedrons, which on cursory inspection, have very much the aspect of cubes: hence the name *cubic saltpetre*. The length of the principal axis is 0·8276. Angle R : R in the terminal edges = 106° 33′. Cleavage very imperfect parallel to R. Specific gravity = 2·24 (Kopp), 2·2256 (Karsten), 2·256 (Schröder). It absorbs water from moist air, and dissolves easily in water, producing considerable fall of temperature. 1 pt. of the salt dissolves in 1·25 pt. water at 0° (Marx), in 1·136 pt. at 18·75° (Karsten), in 1·14 pt. at 1·85° (Kopp). The saturated solution boils at 122° (Kremers). The specific gravities of solutions of nitrate of sodium of various strengths are, according to Schiff (Jahresb. 1858, p. 38), as follows:

| Weight of $NaNO^3$ in 100 pts. water. | Specific gravity of solution at 20·2°. | Weight of $NaNO^3$ in 100 pts. water. | Specific gravity of solution at 20·2°. |
|---|---|---|---|
| 46·48 . . | 1·3806 | 15·50 . . | 1·1075 |
| 30·99 . . | 1·2326 | 10·33 . . | 1·0698 |
| 20 66 . . | 1·1478 | 5·16 . . | 1·0342 |

According to Kremers (*ibid.* 1861, p. 61), the specific gravity at 19·5° of a solution containing 17·7 per cent. nitrate of sodium is 1·1062; for 34·9 per cent., 1·1930; for

51·9 per cent., 1·2640; for 71·7 per cent., 1·3354. **Schiff** (*ibid.* 1861, p. 87) has also determined the solubility of nitrate of sodium in spirit of wine, of various strengths; the results are as follows:

| Weight of anhydrous alcohol in 100 pts. of spirit. | Weight of $NaNO^3$ in 100 pts. of solution saturated at 15°. | Weight of anhydrous alcohol in 100 pts. of spirit. | Weight of $NaNO^3$ in 100 pts. of solution saturated at 15°. |
|---|---|---|---|
| 0 | 45·9 | 40 | 20·5 |
| 10 | 39·5 | 60 | 10·2 |
| 20 | 37·8 | 80 | 2·7 |
| 30 | 26·2 | | |

100 pts. wood-spirit containing 40 per cent. methylic alcohol dissolve 24·4 pts. nitrate of sodium. (**Schiff.**)

[Respecting the solubility of nitrate of sodium in various liquids, see further *Storer's Dictionary of Solubilities*, p. 394.]

Nitrate of sodium melts at a moderate heat (310° according to Person), and solidifies to a white mass on cooling (at 313° according to Schaffgotsch); at a red heat it is decomposed in the same manner as nitrate of potassium, but more easily. It deflagrates with charcoal and other combustible bodies, but not so quickly as nitrate of potassium. On this account, as well as from its hygroscopic character, it cannot be used instead of nitrate of potassium for the manufacture of gunpowder. According to some authorities, however, pure nitrate of sodium is not at all hygroscopic; and indeed, it is sometimes used, after very careful purification, for the preparation of blasting powder, which is not required to burn so quickly as sporting or war powder. It has also been proposed to add anhydrous sulphate of sodium or magnesium to gunpowder prepared with nitrate of sodium, to counteract the hygroscopic tendency. (See *Richardson and Watts's Chemical Technology*, vol. i. pt. 4, p. 435.)

Nitrate of sodium is extensively used for the preparation of nitric acid, and for conversion into nitrate of potassium (p. 100). The crude salt forms an excellent manure for grass land.

**NITRATE OF STRONTIUM.** $SrNO^3$ or $Ssr''N^2O^6$.—Prepared like nitrate of barium. Separates from a hot concentrated solution in anhydrous, from a cold and more dilute solution in hydrated crystals. The *anhydrous* salt crystallises in octahedrons and cubo-octahedrons of sp. gr. 2·305 (**Buignet**), having a cooling pungent taste, soluble in 5 pts. cold, and ½ pt. boiling water; it decrepitates when heated, and melts when red-hot, decomposing at the same time, and leaving a residue of strontia. When thrown on glowing coals it detonates slightly, with a red flame. The *hydrated* salt, $Ssr''N^2O^6.5H^2O$ (**Lanrent**), with $4H^2O$ (**Sonehay** and **Lenssen**, Ann. Ch. Pharm. xcix. 45), also **Ordway** (Jahresb. 1859, p. 115), forms efflorescent crystals belonging to the monoclinic system. Ratio of axes $a : b : c = 0·5895 : 1 : 0·808$. Inclinations of $b$ to $c = 64° 25'$; $\infty P : \infty P$ in the orthodiagonal principal section = 113° 40′; $+ P\infty$ : principal axis = 67° 22′; $oP : \infty P = 76° 20'$. Ordinary combination, $\infty P . oP . + P\infty$ (like fig. 320, CRYSTALLOGRAPHY, ii. 156), or $\infty P . \infty P3 . oP . + P\infty$. Nitrate of strontium is used for the preparation of **red fire**, for which purpose the dried salt is mixed with flowers of sulphur, chlorate of potassium, sulphide of antimony and charcoal.

*Acetonitrate of Strontium*, $S\overset{''}{s}r^2\left\{\begin{matrix}(C^2H^3O)^2\\(NO^3)^2\end{matrix}\right..3H^2O$, crystallises by spontaneous evaporation from a mixed solution of the component salts containing a slight excess of acetic acid in large limpid permanent tabular crystals (v. **Haner**, J. pr. Chem. lxxiv. 432), belonging to the triclinic system, and exhibiting the combination $oP . \infty\breve{P}\infty . \infty\bar{P}\infty . \infty,P . {}'P . \breve{P}'\infty . \tfrac{1}{4}{}'P$. Ratio of axes, $a : b : c = 0·5200 : 1 : 1·1697$. In the left upper octant the angle $a\,c = 77°43'$; $b\,c = 83° 21'$; $a\,b = 88° 19'$. The crystals cleave perfectly parallel to $oP$; less easily parallel to $\infty\breve{P}\infty$. (**Zepharovich**, Wien. Akad. Ber. xli. 517.)

**NITRATE OF TERBIUM.** Radio-crystalline mass, permanent in the air, and dissolving with pale red colour in water.

**NITRATE OF THALLIUM**, $TlNO^3$, crystallises from a solution of thallium in nitric acid in dull white needles, which melt at 205°, with separation of a small quantity of black peroxide. The aqueous solution of the salt thus purified gives no precipitate with ammonia, whereas from the crude solution of thallium in nitric acid, ammonia throws down a small quantity of hydrated peroxide of thallium. Nitrate of thallium has a specific gravity of 5·8, is insoluble in alcohol, but soluble in water, the saturated solution containing 9·75 per cent. salt at 18°, 43·7 per cent. at 58°, and 55·0 per cent. at 100°. (**Crookes**, Chem. Soc. J. xvii. 141.)

**NITRATE OF THORINUM.** $Th''N^2O^6$.—Easily soluble in water and in alcohol. The aqueous solution dries up over oil of vitriol to a crystalline mass; when left to evaporate in the air, it yields a thick syrup (**Berzelius**); according to **Chydenius** (Pogg. Ann. cxix. 43), it crystallises easily. *Nitrate of thorinum and potassium*, $K^2Th''N^4O^{12}$, forms a radiate mass soluble in water and in alcohol. (**Berzelius.**)

**Nitrates of Tin.** Stannic hydrate prepared from the chloride dissolves freely in nitric acid, and if very concentrated acid has been used, the solution deposits *stannic nitrate* in silky scales. If the solution contains nitrate of ammonium, it does not decompose at ordinary temperatures; but in the contrary case, especially if diluted, it deposits stannic hydrate, which redissolves on addition of nitrate of ammonium. Metastannic hydrate (produced by the action of nitric acid on tin) does not dissolve in nitric acid.

*Stannous nitrate* is produced by dissolving stannous oxide, or hydrate, or metallic tin, in cold very dilute nitric acid; the solution is easily decomposed by heat, with separation of stannic hydrate.

**Nitrate of Uranium.** $U^2O^3.N^2O^5.6H^2O$ or *Nitrate of Uranyl* $(UO)'NO^3.3H^2O$.—Produced by treating uranium or either of its oxides with nitric acid. Crystallises in lemon-yellow fluorescent trimetric prisms, in which $a : b : c = 0{\cdot}874 : 1 : 0{\cdot}5703$. Angle $P : P$ (brach.) = 126° 54′ : (macr.) = 118° 30′ : (basal) = 84° 28′ : $\breve{P}\infty : \bar{P}\infty$ (basal) = 62° 40′. Ordinary combination $P . \bar{P}\infty . \infty\breve{P}\infty . \infty\bar{P}\infty$. The crystals effloresce slightly in dry air, and further in a vacuum, giving off half their water. They dissolve in half their weight of water, also in alcohol and ether. The aqueous solution is decomposed at a moderate heat, depositing a lemon-yellow pulverulent substance not yet examined. The crystals melt in their water of crystallisation, then give off water and acid, turn reddish-yellow, and leave pure uranic, or at higher temperatures, uranoso-uranic oxide (Péligot). According to Ordway (Jahresb. 1859, p. 114), the crystallised salt melts at 59·5°, and begins to boil at 118°, the liquid remaining clear till about two-thirds of the water is drawn off, together with a little acid; the residue then becomes somewhat heated in contact with water, and forms a turbid solution which afterwards becomes clear.

**Nitrate of Vanadium.** – *a. Vanadic nitrate.*—Vanadium, vanadious, and vanadic oxide dissolve in nitric acid, forming a blue solution which may be boiled without alteration, but decomposes at a certain degree of concentration, the residue left on evaporating to dryness consisting of vanadic anhydride containing a little nitric acid.—*β. Nitrovanadic acid.* Dilute nitric acid dissolves vanadic acid (or anhydride) with yellowish colour, and on evaporating the solution at ordinary temperatures, a reddish mass is left, from which water extracts a small quantity of nitro-vanadic acid.

**Nitrate of Yttrium.** Large colourless crystals (Berzelius). The solution evaporated at 50° and then quickly cooled, yields colourless laminæ (Berlin). The salt is deliquescent.

**Nitrates of Zinc.** *The normal salt*, $ZnNO^3.3H^2O$ or $Zzn''N^2O^6.6H^2O$ (or $9H^2O$ according to Schindler), separates from highly concentrated solutions in limpid, flattened, striated, four-sided prisms, terminated by four-sided pyramids. They have a sharp taste, deliquesce in the air, dissolve readily in water and in alcohol; melt in their water of crystallisation at 50°, and give off the whole of it in a stream of dry air at 105° (Pierre). According to Graham, half the water goes off at 100°, the remainder only when the salt begins also to part with its acid. According to Ordway, the crystals melt at 36·4°; the liquid boils at 131°, remaining clear during the boiling till it has lost 42 per cent. of its weight; the residue solidifies on cooling to a vitreous mass having nearly the composition $Zzn''O.3Zzn''N^2O^6.3H^2O$. This *tetrazincic salt* was likewise obtained in prismatic needles by Gerhardt (Jahresb. 1847-8, p. 436). Schindler obtained the same salt with only 1 at. water by digesting the octozincic salt with the normal salt. The *octozincic salt*, $7Zzn''O.Zzn''N^2O^6$, is obtained with 2 at. water by heating the normal salt till the fused mass becomes nearly solid (Grenville), or with 4 at. water by precipitating the solution of the normal salt with a quantity of ammonia not sufficient to take up all the nitric acid. (Schindler and Grenville.)

**Nitrate of Zirconium.** The solution of zirconic hydrate in nitric acid yields by evaporation a yellow gummy mass, which has a sour astringent taste, and gives off acid when heated. If it has not been heated above 100°, it redissolves completely in water. The solution is capable of taking up a considerable quantity of zirconic hydrate, forming a soluble basic salt. If the solution thus formed be diluted and heated to boiling, it deposits a still more basic salt in the form of a gelatinous precipitate. A basic salt soluble in water and in alcohol, is likewise obtained by heating the normal salt above 100°.

### *Alcoholic Nitrates. Nitric ethers.*

When nitric acid is heated with an alcohol, part of the alcohol is oxidised, and the nitric acid is reduced to nitrous acid, which, with the remainder of the alcohol, forms a nitrous ether together with other products (p. 75); but by addition of urea or other amide, which decomposes the nitrous acid as fast as it is formed, this action may be prevented and the alcohol and nitric acid will then form a nitric ether.

**Nitrate of Amyl.** *Amyl-nitric ether*, $C^5H^{11}NO^3$.—Prepared by agitating 10 grms. of nitrate of urea with 30 grms. of strong nitric acid in a retort for ten minutes, then adding 40 grms. of amylic alcohol, and gradually heating the mixture, a cooled receiver being adapted to the retort. The distillate, which separates into two layers, is shaken up with water; the lower layer is rectified, the portion which distils from 148° upwards being collected apart; and this portion is rectified twice more, the liquid which goes over at 148° being each time collected apart (W. Hofmann, Ann. Ch. Phys. [3] xxiii. 374). It is also produced by the decomposition of dinitrylide of amylene. (Guthrie, i. 209.)

Nitrate of amyl is a colourless oil of specific gravity 0·994 at 10°, boils at 148° (W. Hofmann); according to Rieckher (Jahrb. pr. Pharm. xiv. 1), it has a specific gravity of 0·902 and boils at 137°. It has an odour of bugs and a sweet burning taste, with very unpleasant aftertaste. It dissolves in ether and alcohol, and is precipitated from the latter by water. Burns with a green-edged flame; is decomposed by alcoholic potash.

**Nitrate of Ethyl.** *Nitric ether. Ethyl-nitric ether*, $C^2H^5NO^3$. *Preparation.*—1. Between 70 and 75 grms. of alcohol of 35° Bm. is distilled with an equal weight of nitric acid of specific gravity 1·40 (or 2 vol. alcohol to 1 vol. nitric acid), and about 2 grams. of nitrate of urea, the receiver being changed as soon as the alcohol which first comes over is replaced by nitric ether, and the distillation stopped as soon as the residue is reduced to one-third of the original mixture. The nitric ether thus obtained is washed with aqueous potash, and afterwards with water, then left for two days in contact with lumps of chloride of calcium, and finally decanted and rectified (Millon, Ann. Ch. Phys. [3] viii. 239). According to Carey Lea (Sill. Am. J. [2] xxxii. 178), it is better to use a larger proportion of nitrate of urea, namely 8 or 10 grms. to the above quantity of liquid; with these proportions larger quantities of liquid may be operated upon at once (see also Heintz, Jahresb. 1863, p. 482).—2. According to J. Persoz (Rép. Chim. pure, v. 30), nitrate of ethyl is easily obtained, without the use of urea, by dropping absolute alcohol (10 grms.) from a very fine pipette into highly concentrated colourless nitric acid (about 20 grms.) contained in a platinum dish, well cooled with a mixture of ice and salt. The formation of the ether takes place as the liquids mix. A lump of ice is then to be thrown into the mixture, whereby the acid is diluted without rise of temperature. If any oxidation of the alcohol takes place from dropping it in too quickly—which may be known by the emission of red fumes—a piece of ice must be immediately dropped in to save the ether already formed, and the operation repeated.

*Properties.*—Nitric ether is a liquid of specific gravity 1·112 at 17°, boiling at 85° or 86°. Its vapour-density at 85·5° = 3·112; at 90° = 3·094; at 70·3° = 3·065; at 64·9° = 3·079 (Playfair and Wanklyn). It has an odour different from that of nitrous ether, and a very sweet taste, with bitterish aftertaste. It is insoluble in water, but mixes in all proportions with alcohol and ether. It burns with a white flame; its vapour, if heated above the boiling point, explodes violently when set on fire.

Heated to 100° with *alcoholic ammonia*, it yields nitrate of ethylamine (Juncadella, Compt. rend. xlviii. 342):

$$C^2H^5NO^3 + NH^3 = C^2H^7N.HNO^3.$$

When a mixture of equal volumes of nitric ether, alcohol and strong aqueous ammonia is heated to 100° in a sealed tube only two-thirds filled with it, the ether disappears completely, and the resulting solution contains di- and tri-ethylamine together with ethylamine and ammonia. With a considerable excess of ammonia, the nitric ether may be decomposed even without alcohol. (Carey Lea, Sill. Am. J. [2] xxxii. 25.)

Nitric ether is easily reduced by *sulphide of ammonium* in alcoholic solution, yielding mercaptan, according to the equation,

$$C^2H^5NO^3 + 5H^2S = C^2H^6S + NH^3 + 3H^2O + S^4.$$

(E. Kopp, J. Pharm. [3] xi. 321). Heated with *ferrous acetate* it is gradually resolved into nitrogen gas, a small quantity of nitrous ether and ammonia. (Carey Lea.)

*Mercurethylic Nitrate.* $C^2H\overset{\prime\prime}{hg}{}^3N^2O^6$ or $C^4H\overset{\prime\prime}{hg}{}^5N^2O^6.Hhg''N^2O^6$. *Ethylo-mercuric nitrate. Salpetersaures Aethyl-Quecksilberoxyd. Nitrate d'éthyle et de mercure.*—This compound, discovered by Sobrero and Selmi (Compt. rend. xxxiii. 67), and further examined by Gerhardt (Chem. Soc. Qu. J. v. 88), is obtained by mixing alcohol with excess of a very strong solution of trimercuric nitrate. No precipitate is formed in the cold, but on heating the liquid, a white crystalline compound separates even before the boiling point is attained, and its formation continues without further application of heat. The reaction is as follows:

$$Hhg^3N^2O^8 + C^2H^6O = C^2Hhg^3N^2O^6 + 3H^2O.$$

The alcoholic mother-liquor contains a large quantity of mercurous nitrate. A mercurous salt, probably formed by secondary actions, frequently also separates in small needles after the mercurethylic nitrate has been removed by decantation.

Mercurethylic nitrate is a white crystalline salt which, when examined by the microscope, exhibits a highly characteristic form, consisting of six-pointed stars or hexagonal tables, shaded on the edges in such a manner that similar stars appear within them, with their vertices projecting into the angles of the tables. The crystals gave by analysis 2·9 per cent. carbon, 3 hydrogen, 78·4 mercury, and 3·6 nitrogen (Gerhardt), agreeing with the formula $C^2Hhg^3NO^6.H^2O$, which requires 3·1 carbon, 0·3 hydrogen, 78·3 mercury, 3·3 nitrogen and 15·0 oxygen.

Mercurethylic nitrate is insoluble both in *water* and in *alcohol*. Heated in a small tube it decomposes suddenly and explosively, but without detonation.—*Hydrochloric acid* dissolves it completely, without leaving a trace of calomel; hence it is a mercuric and not a mercurous salt. The hydrochloric acid solution gives a yellow precipitate with potash.—*Sulphydric acid* decomposes the salt, forming sulphide of mercury and a substance having the odour of mercaptan. A strong aqueous solution of *potash* turns the salt grey; when boiled with the same solution, it turns black, but is not completely decomposed; the black substance is always mixed with crystals, however long the boiling may be continued. Hydrochloric acid does not dissolve this black substance, though it forms but a small quantity of calomel. It appears therefore that the salt is essentially altered by the action of the potash.—*Ammonia* acts upon it in a similar manner.

NITRATE OF METHYL. *Methyl-nitric ether.* $CH^3NO^3$.—This ether is easily obtained by dissolving 40 grms. of nitrate of urea in 200 cub. cent. of pure methylic alcohol, adding 150 cub. cent. of pure nitric acid of specific gravity 1·31 (free from nitrous acid so that it gives no colouring with ferrous sulphate), and distilling to one-third. This process is to be twice repeated, the residue being mixed in the first instance with 170 c. c. methylic alcohol and 130 c. c. nitric acid, and in the second with 150 c. c. methyl-alcohol, 110 c. c. nitric acid, and 10 grms. nitrate of urea. The distillate is washed, first with solution of common salt, then with dilute carbonate of sodium. By this process 420 grms. methylic alcohol yield 300 grms. crude nitrate of methyl. (Carey Lea, Sill. Am. J. [2] xxxiii. 227). Dumas and Péligot (Ann. Ch. Phys. [2] lviii. 37), by distilling wood-spirit with saltpetre and oil of vitriol, obtained a liquid boiling at 66°, which appears to have been a mixture of nitrate and nitrite of methyl, as its analysis gave about 3 per cent. too much carbon for the formula of the nitrate. The vapour exploded with great violence when heated to about 150°. The properties of the pure nitrate of methyl obtained by Lea have not been described.

NITRATE OF OCTYL. $C^8H^{17}NO^3$. *Nitrate of Capryl.*—Produced by decomposing iodide of octyl dissolved in alcohol with nitrate of silver. Oily liquid which has a fruity odour, floats on water, is insoluble in alcohol, boils with decomposition, burns with a bright flame, and is decomposed by alcoholic potash, yielding octylic alcohol and nitrate of potassium. (Bouis, Ann. Ch. Phys. [3] xlix. 136.)

**NITROGEN, PHOSPHIDES OF.** $NP'''$. See PHOSPHOROSAMIDES.

**NITROGEN, SULPHIDE OF.** NS. (Fordos and Gélis, Ann. Ch. Phys. [3] xxxii. 389.)—This compound, the analogue of nitric oxide, is obtained by passing ammoniacal gas through a solution of protosulphide of chlorine in disulphide of carbon. Sal-ammoniac is first precipitated, and then a dark brown flaky substance, which is decomposed by the further action of the ammonia. The passage of the gas must be continued till the brown flakes have almost disappeared, and an orange-yellow liquid is formed, which may be separated from the chloride of ammonium by filtration and obtained quite clear. The filtrate, when left to evaporate, first deposits sulphur and afterwards crystals of sulphide of nitrogen. The reaction is very complicated, but the final result may be represented by the equation:

$$3Cl^2S + 8NH^3 = 2NS + S + 6NH^4Cl.$$

Sulphide of nitrogen crystallises in transparent golden-yellow rhombic prisms with dihedral summits. It has a faint odour, adheres strongly to paper if rubbed upon it, and produces painful irritation of the mucous membrane of the nose and eyes. It explodes by percussion or when heated to 150°—160°. It dissolves very sparingly in alcohol, ether, and sulphide of carbon: water does not dissolve, but slowly decomposes it. Its solution in sulphide of carbon also undergoes slow decomposition. It unites in several proportions with the sulphides of chlorine.

**NITROGENIUM.** Syn. with NITROGEN.

**NITROGENTIANIC ACID.** See GENTIANIC ACID (ii. 830).

**NITROGLYCERIN.** See GLYCERIN (ii. 890).

**NITROHARMALINE.** See Harmaline (iii. 9).

**NITROHARMINE** or **NITROHARMIDINE.** See Harmine (iii. 11).

**NITRO-HÆMATIC ACID.** Syn. with Picramic Acid.

**NITROHELENIN.** See Helenin (iii. 138).

**NITROHIPPURIC ACID.** See Hippuric Acid (iii. 161).

**NITROHUMIC ACID.** See Ulmic Acid.

**NITROHYDURILIC ACID.** See Hydurilic Acid (iii. 221, footnote).

**NITRO-INOSITE.** See Inosite (iii. 276).

**NITRO-IODIC ACID** or **ANHYDRIDE.** See Iodic Acid (iii. 299).

**NITROLACTIN.** See Milk-Sugar (iii. 1024).

**NITROLEUCIC ACID.** Syn. with Nitrate of Leucine. (See Leucine, iii. 582.)

**NITROMANNITE.** See Mannite (iii. 825).

**NITROMECONIN.** See Meconin (iii. 863).

**NITROMELANILINE.** See Melaniline under Phenylamines

**NITROMESIDINE.** See Mesitylene (iii. 930).

**NITROMESITYLENES.** See Mesitylene (iii. 930).

**NITROMETACETONIC ACID.** Syn. with Nitro-Propionic Acid. (See Propionic Acid.)

**NITROMETHIDES.** This name may be applied to certain compounds derivable from marsh-gas (hydric methide) by the substitution of one or more molecules of nitryl for an equivalent quantity of hydrogen. Their names and formulæ are given in the following table, in which nitryl ($NO^2$) is denoted by X.

Type, C H H H H.

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | Tribromonitromethide, Nitro-bromoform or Bromopicrin . | C | X | Br | Br | Br |
| 2. | Trichloronitromethide, Nitrochloroform or Chloropicrin . | C | X | Cl | Cl | Cl |
| 3. | Trinitromethide or Nitroform . . . . . . . | C | X | X | X | H |
| 4. | Bromotrinitromethide or Bromonitroform . . . | C | X | X | X | Br |
| 5. | Tetranitromethide . . . . . . . . | C | X | X | X | X |
| 6. | Cyanonitromethide, Nitracetonitrile or Fulminic acid . | C | X | H | H | Cy |
| 7. | Cyanodinitromethide or Dinitracetonitrile . . . | C | X | X | H | Cy |
| 8. | Cyanotrinitromethide or Trinitracetonitrile . . . | C | X | X | X | Cy |
| 9. | Cyano-dibromo-nitromethide or Dibromo-nitracetonitrile . | C | X | Br | Br | Cy |

The first and second of these compounds have been already described as Bromopicrin and Chloropicrin (i. 923).

3. **Nitroform.** $C(NO^2)^3H$.—This compound discovered by Schischkoff (Ann. Ch. Pharm. ciii. 364) exhibits the relations of an acid. Its ammonium-salt, $C(NO^2)^3NH^4$, is obtained as a yellow crystallisable substance, soluble in water and in alcohol, by the action of water or alcohol on cyanotrinitromethide (p. 111); and on agitating this salt with strong sulphuric acid, the nitroform is separated and floats on the surface of the liquid, in the form of an oil which may be removed.

Nitroform, at temperatures above 15°, is a colourless oil; below that temperature it solidifies in colourless cubic crystals. It is moderately soluble in water, forming a dark yellow solution. It cannot be distilled, as it explodes with violence when heated.

The atom of hydrogen in nitroform may be replaced either by metals or by chlorous radicles, namely bromine and nitryl. The metallic derivatives or *salts of nitroform*, are for the most yellow and crystallisable: they explode when heated.

4. **Bromonitroform.** $C(NO^2)^3Br$.—Produced by exposing nitroform to the action of bromine for some days under the influence of direct sunshine, or more easily by treating an aqueous solution of mercuric nitroform, $C^2(NO^2)^6Hhg''$, with bromine. It is colourless, liquid above + 12°, but solidifies below that temperature to a white crystalline mass. It is somewhat soluble in water, and may be distilled with aqueous vapour, or in a current of air. It decomposes at 140°. (Schischkoff, Ann. Ch. Pharm. cxix. 247.)

5. **Tetranitromethide.** *Tetranitrylide of Carbon. Nitro-kohlenstoff.* $C(NO^2)^4$.—Produced by treating nitroform with fuming nitric and sulphuric acids, heating the liquid to 100° and passing air through it. A liquid then distils over, from which water throws down tetranitromethide as a heavy oil.

Tetranitromethide is liquid at ordinary temperatures, but solidifies at + 13° to a white crystalline mass. It is insoluble in water, but soluble in alcohol and ether. It boils at 126°, and unlike nitroform, may be distilled without decomposition. When rapidly heated, it decomposes with evolution of nitrous vapours; but even then it does not explode. It does not take fire by contact with flame; but a glowing coal on which it is poured burns with a bright light. (Schishkoff.)

6. **Cyanonitromethide** or **Nitracetonitrile** does not exist in the free state, but its salts, the FULMINATES, already described (ii. 730), give rise by their decomposition to the three following compounds, cyano-dibromo-nitromethide being produced by the action of bromine on fulminate of mercury, while cyanodinitromethide and cyanotrinitromethide are obtained from fulminuric acid (ii. 739) which is itself a product of the decomposition of fulminate of silver.

7. **Cyanodinitromethide** or **Dinitracetonitrile.** $C^2HN^3O^4 = C(NO^2)^2HCy = C^2(NO^2)^2HN$. (Schischkoff and Rosing, Ann. Ch. Pharm. civ. 249; Schischkoff, *ibid.* cxix. 249.)—This compound is an acid, the ammonium-salt of which (originally called *dinitrammonyl*) is obtained by the action of sulphydric acid on cyanotrinitromethide;

$$C(NO^2)^3Cy + 4H^2S = C(NO^2)^2(NH^4)Cy + S^4 + 2H^2O.$$

On mixing the aqueous solution of this ammonium-salt with an equivalent quantity of sulphuric acid, agitating with ether, and evaporating the ethereal solution, a syrup is left which gradually yields large crystals of cyanodinitromethide, apparently containing water of crystallisation.

Cyanodinitromethide treated with ammonia reproduces the original ammonium-salt, which crystallises in colourless needles, easily soluble in water, sparingly in alcohol, insoluble in ether. When boiled with oxide of silver, it forms a solution which on cooling deposits crystals of the *argentammonium-salt* of cyanodinitromethide, $C(NO^2)^2(NH^3Ag)Cy$.

Cyanodinitromethide also forms crystalline salts with potassium and with silver. The *silver-salt*, $C(NO^2)^2AgCy$, detonates like fulminate of silver, and is decomposed by bromine, yielding an oily body, probably *cyanobromodinitromethide*, $C(NO^2)^2BrCy$.

8. **Cyano-trinitromethide** or **Trinitracetonitrile.** $C^2N^4O^6 = C(NO^2)^3Cy = C^2(NO^2)^3N$. (Schischkoff, Ann. Ch. Pharm. ci. 213).—When a salt of fulminuric acid is added by small portions to a cooled mixture of highly concentrated nitric and sulphuric acids, carbonic anhydride is evolved, and trinitracetonitrile separates as an oil which crystallises on cooling:

$$\underset{\text{Fulminuric acid.}}{C^3(NO^2)H^3N^2O} + 2NO^3H = CO^2 + H^2O + NH^3 + \underset{\text{Trinitracetonitrile.}}{C^2(NO^2)^3N}.$$

Cyanotrinitromethide is a white crystalline camphor-like substance, melting at 41·5°, and decomposing with explosion at 220°. It may be distilled in a current of air at 60°. It dissolves without alteration in *ether*, but is decomposed by *water* and *alcohol* even in the cold, and more quickly when heated, into carbonic anhydride and the ammonium-salt of nitroform:

$$C^2(NO^2)^3N + 2H^2O = CO^2 + C(NO^2)^3(NH^4).$$

*Sulphydric acid* converts it into the ammonium-salt of cyanodinitromethide (p. 110).

9. **Cyano-dibromonitromethide** or **Dibromonitracetonitrile.** $C^2Br^2N^2O^2 = C(NO^2)Br^2Cy = C^2(NO^2)Br^2N$ (Kekulé, Ann. Ch. Pharm. cv. 281).—This compound, which differs from mercuric fulminate, $C^2Hg''N^2O^2$, only by containing 2 at. bromine in place of 1 at. mercury, is prepared by pouring bromine on mercuric fulminate under water till the colour of the bromine is no longer destroyed. On subsequently distilling the liquid, cyanodibromonitromethide passes over with the aqueous vapour, in the form of an oil which partly solidifies in the crystalline form.

Cyano-dibromonitromethide forms large well-defined crystals, insoluble in water, soluble in alcohol and in ether, and smelling like chloropicrin. It melts at 50°, and begins to boil, with decomposition, between 130° and 135°. With vapour of water it may be distilled without decomposition (Kekulé). When gently heated with iron-filings and acetic acid, it is strongly attacked, giving off hydrocyanic acid, hydrobromic acid, ammonia, and probably also carbonic anhydride. (Stahlschmidt, Jahresb. 1860, p. 241.)

**NITROMETHYLIC ACID (DI-).** $CH^4N^2O^2$ or $C^2H^8N^4O^4$. (Frankland, Phil. Trans. 1857, p. 59; Chem. Soc. Qu. J. xi. 88.)—This acid, homologous with dinitro-ethylic acid (p. 61) is obtained, similarly to the latter, by the action of nitric oxide on zinc-methyl, 4 at. of the former uniting with 2 at. of the latter to form the salt, $C^2H^6Zn''N^4O^4.C^2H^6Zn''$. This *salt* is decomposed by water, yielding marsh-gas and *basic dinitromethylate* or *oxy-dinitromethylate of zinc*, $C^2H^6Zn''N^4O^4.Zn''O$; which, when decomposed by carbonic acid, yields the *normal zinc-salt*, $C^2H^6Zn''N^4O^4.H^2O$.—The *sodium-salt*, $CH^3NaN^2O^2.H^2O$, is obtained by treating a solution of the normal zinc-salt with carbonate of sodium, evaporating to dryness, and

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exhausting the residue with strong alcohol. It is very soluble in water and in alcohol, and burns intensely when heated.

**NITRO-MURIATIC ACID.** *Aqua regia. Königswasser.*—A yellow fuming liquid produced by mixing strong nitric and hydrochloric acids. The mixture is at first colourless; but after a short time, or quickly if heated, it assumes a deep orange-yellow colour, and breaks up into water, chlorine and the chlorides of nitrosyl, chiefly the dichloride. The dilute acids may remain mixed for a long time without decomposing each other, unless heat is applied. Nitro-muriatic acid dissolves gold and platinum, an action which seems to depend entirely on the presence of the chlorine liberated by the mutual action of the original acids. The same reaction renders nitromuriatic acid very useful in destroying organic matter, in toxicological investigations for example (see Arsenic, i. 366). An impure nitromuriatic acid is prepared by dissolving nitrate of sodium in hydrochloric acid, or chloride of sodium in nitric acid.

**NITRONAPHTHALENES.** See Naphthalene (p. 14).

**NITRONAPHTHYLAMINE.** See Naphthylamine (p. 21).

**NITRO-OXYBENZOIC ACID.** See Oxybenzoic Acid.

**NITROPAPAVERINE.** See Papaverine.

**NITROPEUCEDAMIDE** and **NITROPEUCEDANIN.** See Peucedanin.

**NITROPETROL-DIAMINE.** See Petrol.

**NITROPHENAMIC ACID.** *Dinitro-diphenamic acid.* $C^{12}H^{12}N^4O^{12} = C^{12}H^{12}(NO^2)^2N^2O^2$. (Laurent and Gerhardt, Compt. Chim. 1849, p. 468.)—An acid produced by the action of sulphydrate of ammonium on dinitrophenic acid:

$$2C^6H^4(NO^2)^2O + 3(NH^4)^2S^1 = C^{12}H^{12}(NO^2)^2N^2O^2 + 4H^2O + S^3.$$

It forms brown hexagonal needles, with four angles of 131° 30′ and two of 97°, containing 2 at. water, which they give off between 100° and 110°, the anhydrous acid decomposing at a higher temperature; they yield a yellow powder. The acid is sparingly soluble in cold water, moderately soluble in *alcohol* and *ether*. It dissolves in *ammonia*, forming a deep red solution which is decomposed by concentration, with evolution of ammonia. With aqueous *potash*, it yields the salt $C^{12}H^{11}K(NO^2)^2N^2O^2$, which crystallises in dark red nodules, very soluble in water and in alcohol. The *barium-salt* forms sparingly soluble brown-red needles obtained by precipitating acetate of barium with an ammoniacal solution of the acid. The *calcium-salt* is gradually precipitated in like manner in small needles. The *copper-salt* is a yellowish-green, the *lead-salt* an orange-brown precipitate. The *silver-salt*, $C^{12}H^{11}Ag(NO^2)^2N^2O^2$, is a dark brown-yellow precipitate which crystallises in scales from hot solutions.

**NITROPHENAMYLIDINE** or *Amyl-nitro-phenidine.*—A base formed by the action of alcoholic sulphydrate of ammonium on the heavy oil obtained by treating phenate of amyl (*q. v.*) with fuming nitric acid. It is crystallisable and forms crystallisable salts. (Cahours, Compt. rend. xxxii. 61.)

**NITROPHENESIC ACID.** Syn. with Dinitrophenic Acid. (See Phenol.)

**NITROPHENETOL.** Syn. with Nitrophenate of Ethyl. (See Phenic Ethers, under Phenol.)

**NITROPHENIC ACIDS.** See Phenol, Derivatives of.

**NITROPHENISIC ACID.** Syn. with Tri-nitrophenic Acid. (See Phenol.)

**NITROPHENOIC ACID.** See Phenoic Acid.

**NITROPHENOL.** See Phenol.

**NITROPHENYLAMINE.** See Phenylamine.

**NITROPHENYL-CARBAMIDES.** See Carbamides (i. 756).

**NITROPHENYLENE-DIAMINE.** See Phenylene-diamines.

**NITROPHENYL-PHOSPHORIC ACID.** See Phosphoric Ethers.

**NITROPHENYL-PYROTARTRAMIC ACID.** See Pyrotartramic Ethers.

**NITROPHENYL-SULPHURIC** and **SULPHUROUS ACIDS.** See Sulphuric and Sulphurous Ethers.

**NITROPHLORETIN.** See Phloretin.

**NITROPHLOROGLUCIN.** See Phloroglucin.

**NITROPHTHALENE.** $C^8H^7(NO^2)$. (Dusart, Ann. Ch. Phys. [3] xliv. 332.) —A compound, isomeric with nitro-cinnamene, formed by the action of potash on nitronaphthalene. To prepare it, 2 pts. of caustic potash dissolved in as little water as possible are mixed with 1 pt. of fresh slaked lime, to which nitronaphthalene is gradually added. The action begins almost immediately, the mixture becoming reddish. The mass is kept for about six hours at a temperature not exceeding 100°, and is stirred from time to time, the evaporated water being replaced; the whole is then added to a large quantity of water and allowed to settle down; the alkaline solution, coloured deep yellow by nitrophthalinic acid, is decanted off; and the deposit is washed with water until the latter is only slightly coloured. The lime is removed from the brown residue by dilute hydrochloric acid, and the remainder thrown on a filter and washed with water. The nitrophthalene can only be separated from the brown matter with which it is mixed by distilling with steam; it then passes over in oily drops which crystallise on cooling. If distilled alone, the product is less pure.

Nitrophthalene is of a straw-yellow colour and crystallises on cooling from hot alcohol in long needles, which are tasteless and have a faint odour. It melts at 48°, begins to boil at 280°, and distils over in large quantities between 300° and 320°, leaving a slight carbonaceous residue. It is not soluble in cold water, but when distilled with water, imparts to it an aromatic odour and separates on cooling in needles having a silky lustre. It is but slightly soluble in cold *alcohol*, but readily in hot alcohol; dissolves abundantly in *ether* and in *coal-oil*.

Nitrophthalene heated with a strong solution of *potash*, yields nitrophthalic acid; less readily with hydrate of calcium or barium. When distilled with dry *potash-lime*, it evolves much ammonia, while an odorous oil distils over, and the sides of the retort become covered with long yellow needles which dissolve in sulphuric acid with a beautiful violet-blue colour. The oil is slightly soluble in water, and the solution gives with ferric salts an indigo-blue precipitate. *Sulphide of ammonium* converts nitrophthalene into phthaldine, sulphur separating out:

$$C^8H^7NO^2 + 3H^2S = C^8H^9N + 2H^2O + S^3.$$

**NITROPHTHALIC ACID.** See PHTHALIC ACID.

**NITROPHTHALAMIDE.** See PHTHALAMIDES.

**NITROPHTHALINIC ACID.** $C^8H^7(NO^2)O^3$? (Dusart, *loc. cit.*)—This acid is formed in the preparation of nitrophthalene as above described, and is precipitated from its aqueous solution by hydrochloric acid, in golden flocks, which, by solution in a mixture of 1 pt. water and 2 pts. alcohol of 36°, may be obtained in stellate groups of golden-yellow needles. It is inodorous and tasteless at first, but leaves a pungent after-taste. When heated in a tube, it melts, gives off an odour of cyanide of ammonium, and leaves a large quantity of charcoal. It is sparingly soluble in *water*, more soluble in *alcohol*. Its ammoniacal solution forms yellow precipitates with salts of *calcium* and *barium*; greenish-yellow with *cupric salts*; red with *silver-salts*. The *lead-salt* is precipitated in orange-yellow flocks, which when dry, explode by heat, or by contact with oil of vitriol. The *potassium-salt* forms reddish-yellow mammillated crystals, very soluble in water; the solution possesses great colouring power.

**NITROPIANYL.** Syn. with NITROMECONIN. (See MECONIN, iii. 803.)

**NITROPICRIC ACID.** Syn. with PICRIC or TRINITROPHENIC ACID.

**NITROPICROTOXINE.** See PICROTOXINE.

**NITROPROPIONIC ACID.** See PROPIONIC ACID.

**NITROPRUSSIDES** or NITROPRUSSIATES. Syn. with NITROFERRICYANIDES. (See CYANIDES OF IRON, ii. 250.)

**NITROPYRENE.** See PYRENE.

**NITRORACEMIC ACID.** See RACEMIC ACID.

**NITROSACCHAROSE.**—A substance formed by the action of fuming nitric acid (Sobrero), or of a mixture of nitric and sulphuric acids (Schönbein, Reinsch) on cane-sugar. It is a white transparent resin, friable in the cold, but at ordinary temperatures soft, glutinous, and ropy. It is neutral, inodorous and bitter; melts at about 30° (Reinsch). It is insoluble in cold *water*, but melts to an oil and slowly dissolves in boiling water; the solution gives the reactions of nitrites (Schönbein). It dissolves freely in *alcohol*, *ether*, and *fixed oils*. It explodes when heated on platinum foil or by percussion; and deflagrates when touched with a glowing splinter (Reinsch). When heated with solid caustic *potash*, it froths up, blackens and then takes fire (Schönbein). See *Gmelin's Handbook*, xv. 295.

**NITROSALICYLAMIDE.** See SALICYLAMIDES.

**NITROSALICYLIC ACID.** See SALICYLIC ACID.

**NITROSALICYLIDES.** See SALICYLOUS ACID, DERIVATIVES OF.

**NITROSO-COMPOUNDS.**—Bodies formed by the substitution of the monatomic radicle, NO, for an equivalent quantity of hydrogen; thus nitrous acid, $HNO^2$, may be regarded as $\left.\begin{array}{c}NO\\H\end{array}\right\}O$, that is as a molecule of water, in which half the hydrogen is replaced by nitrosyl; and similarly for all the nitrites.

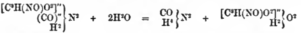
**NITROSETHYLIN.** $C^4H^{10}N^2O = C^4H^{10}(NO)N$. (Genther and Krentzhage, Ann. Ch. Pharm. cxxvii. 43.)—This body, which has the composition of diethylamine, $C^4H^{11}N$, in which 1 at. hydrogen is replaced by nitrosyl, is produced by the action of nitrite of potassium on hydrochlorate of diethylamine:

$$C^4H^{11}N + HNO^2 = C^4H^{10}N^2O + H^2O.$$

The materials are distilled together at a gentle heat; the nitrosethylin is freed from diethylamine by redistilling the liquid after neutralisation with sulphuric acid; the sulphate of diethylamine which remains is completely converted into nitrosethylin by repeated treatment with nitrite of potassium; and the nitrosethylin, after dehydration with chloride of calcium, is rectified in a stream of carbonic anhydride, the portion which distils at about 176° being collected apart.

Nitrosethylin is an oily liquid of faint yellowish colour, peculiar aromatic odour, and burning taste. It has a specific gravity of 0·951 at 17·5°, and boils at 176·9°. When exposed to the *air*, it gradually turns brown. It dissolves in strong *hydrochloric acid*, forming a dark coloured liquid, which is decomposed by heat, giving off nitric oxide and leaving hydrochlorate of diethylamine. The reaction is evidently the reverse of that by which nitrosethylin is formed (see the above equation), the nitrous acid first set free being immediately resolved into nitric oxide and nitric acid. Nitrosethylin absorbs *hydrochloric acid gas*, forming a thick liquid, in which, after the excess of hydrochloric acid has been removed by a stream of carbonic anhydride, crystals are formed, which dissolve easily in water. The action of *chlorine* on nitrosethylin also gives rise to crystalline products.

**NITROSO-MALONIC ACID.** $C^3H^3NO^5 = C^3H^3(NO)O^4$. (Baeyer, Ann. Ch. Pharm. cxxxi. 293.)—This acid is produced, not directly from malonic acid (iii. 799), but by the action of potash on violuric acid, $C^4H^3N^3O^4$, which is itself produced by the action of nitrous acid on barbituric acid (malonyl-carbamide, $CH^2(C^3H^2O^2)''N^2O$), and has the composition of nitroso-malonyl-carbamide, $CH(NO)(C^3H^2O^2)''N^2O$ (see URIC ACID, DERIVATIVES OF). The reaction is as follows:



$$\left.\begin{array}{r}[C^3H(NO)O^2]''\\(CO)''\\H^2\end{array}\right\}N^2 + 2H^2O = \left.\begin{array}{r}CO\\H^4\end{array}\right\}N^2 + \left.\begin{array}{r}[C^3H(NO)O^2]''\\H^2\end{array}\right\}O^2$$

Nitroso-malonyl-carbamide. Carbamide Nitroso-malonic acid.

Malonic acid is produced from barbituric acid in a precisely similar manner.

To prepare the acid, violurate of potassium is warmed with potash-ley of specific gravity 1·2; the brownish liquid is decolorised by addition of a slight excess of acetic acid and a few drops of alcohol, then filtered and mixed with about twice its volume of alcohol; the nitroso-malonate of potassium, which first separates in oily drops and then crystallises, is converted into a silver-salt; and this last is decomposed with hydrochloric acid. The solution thus obtained yields nitroso-malonic acid, by evaporation in vacuo, in shining prismatic needles, very soluble in water, and containing water of crystallisation which they give off over oil of vitriol. The aqueous solution begins to decompose when gently heated, and is completely resolved at the boiling heat into prussic acid, carbonic anhydride and water:

$$C^3H^3(NO)O^4 = CNH + 2CO^2 + H^2O.$$

The dry acid heated on platinum-foil, first melts, and then decomposes with a sharp report.

Nitroso-malonic acid is dibasic, but only neutral salts of it have been obtained; the nitroso-malonates of the alkali-metals dissolve readily in water, but are precipitated by alcohol; those of the earth-metals and heavy metals are insoluble or sparingly soluble, and may be obtained by precipitation.

The *potassium-salt*, $C^3HK^2(NO)O^4$, is precipitated from its aqueous solution by alcohol, in oily drops which soon solidify if the alcohol be quickly added, in larger laminæ by slower precipitation. The *lead-salt* is a crystalline precipitate containing $C^3HPpb''(NO)O^4.2H^2O$. The *silver-salt*, $C^3HAg^2(NO)O^4.H^2O$, is obtained as an amorphous precipitate which soon becomes crystalline. It is blackened by light, dissolves easily in nitric acid and in ammonia, and does not part with its water of crystallisation at 110°.

The soluble salts of nitroso-malonic acid give a red colouring with *ferric chloride*, and a dark olive-green precipitate with *cupric salts*.

**Amidomalonic acid,** $C^3H^3(NH^2)O^4$. A product of the reduction of nitroso-malonic acid by sodium amalgam:

$$C^3H^3(NO)O^4 \quad + \quad H^4 \quad = \quad C^3H^3(NH^2)O^4 \quad + \quad H^2O.$$

It crystallises from aqueous solution, by evaporation in vacuo, in rather large, ill-defined, shining prisms; by precipitation with alcohol in needles. The crystals contain water, which they gradually lose over oil of vitriol. The acid melts when heated, giving off carbonic anhydride, and leaving a residue of glycocine:

$$C^3H^5NO^4 \quad = \quad CO^2 \quad + \quad C^2H^5NO^2.$$

The same decomposition takes place on warming the aqueous solution.

Amidomalonic acid is quickly decomposed by oxidising agents. When *iodine* is added to an aqueous solution of the acid containing a small quantity of iodide of potassium, the product is mesoxalic acid (iii. 932).

$$\underset{\substack{\text{Amidomalonic}\\ \text{acid.}}}{C^3H^5NO^4} \quad + \quad H^2O \quad + \quad I^2 \quad = \quad \underset{\substack{\text{Mesoxalic}\\ \text{acid.}}}{C^3H^2O^5} \quad + \quad HI \quad + \quad NH^4I$$

The amidomalonates of the *alkali-metals* are easily soluble in water and are precipitated in crystals by alcohol. The other amidomalonates are sparingly soluble crystalline precipitates. The *barium-* and *calcium-salts* dissolve with tolerable facility in hot water, and crystallise therefrom. The *copper-salt* is a white-green precipitate. The potassium-salt mixed with cupric acetate appears to form a blue double salt. The alcoholic solution of the acid heated with cupric salts, throws down cuprous oxide. The *lead-* and *silver-salts* are crystalline precipitates. The acid appears to be monobasic, forming with neutral acetate of lead only one salt containing $C^3H^4PbNO^4$ or $C^6H^8Pb''N^2O^8$.

**NITROSONAPHTHALIN.** $C^{10}H^6(NO)N$? Perkin and Church (Chem. Soc. Qu. J. ix. 1; Jahresb. 1856, p. 607), by the action of nascent hydrogen on dinitronaphthalene, and by that of nitrous acid on naphthylamine, or of nitrite of potassium on hydrochlorate of napththylamine, obtained a dark coloured crystalline substance to which they assigned the above name and formula. But from subsequent researches on the action of nitrite of potassium on salts of napththylamine (Chem. Soc. J. xvi. 207), they conclude that the product formerly obtained was not a definite compound, but a mixture of two or more different substances, and that when proper precautions are taken to ensure a definite reaction, the product consists essentially of azodinaphthyldiamine, $C^{20}H^{15}N^3$ (p. 23); they are also of opinion that the body formerly described by them as nitrosonaphthalin has no existence. Considering however that this supposed body is exactly analogous in composition and mode of formation to nitrosethylin and nitrosophenylin, and that the reaction by which it was originally obtained is said to have given rise to the formation of more than one compound, its existence cannot perhaps be regarded as completely disproved. The action of nascent hydrogen on dinitronaphthalene, by which nitrosonaphthalin was first obtained, does not appear to have been re-examined.

**NITROSOPHENYLIN.** $C^6H^6N^2O = C^6H^6(NO)N$. Perkin and Church (Chem. Soc. Qu. J. ix. 1).—This substance, which is analogous in composition to nitrosethylin and nitrosonaphthalin, and may be regarded as phenylamine ($C^6H^7N$), in which 1 at. H is replaced by NO, is obtained by the action of nascent hydrogen on dinitrobenzene. When a piece of pure zinc is immersed in a cold saturated alcoholic solution of dinitrobenzene, and strong hydrochloric acid is gradually added, the evolution of hydrogen soon ceases, and the liquid gradually acquires a crimson colour. At the end of the reaction, the zinc is to be taken out, the liquid completely neutralised with alkali, and the dark coloured zinc-oxide repeatedly washed with strong alcohol. The alcoholic solution when evaporated, leaves nitrosophenylin, which may be purified by washing with water, re-solution in alcohol, and evaporation over the water-bath.

Nitrosophenylin is a black, shining, brittle substance, which melts when heated, and then decomposes; is nearly insoluble in *water*, very slightly soluble in *benzene*, easily soluble in *acids* and in *alcohol*. An alcoholic solution containing only 0·2 per cent. nitrosophenylin appears opaque and of a shining orange-red colour by reflected light. Strong *hydrochloric* or *sulphuric acid* dissolves nitrosophenylin with a splendid crimson colour; boiling *nitric acid*, with yellow; *fuming sulphuric acid*, with brown colour. *Alkalis* precipitate it from its acid solutions without alteration, at least if they act for a short time only. By the prolonged action of *nascent hydrogen*, nitrosophenylin is converted into a colourless substance not containing oxygen. When heated with *soda-lime* it gives off all its nitrogen as ammonia and aniline.

**NITROSO-PIPERIDINE.** See PIPERIDINE.

**NITROSO-SULPHATES,** commonly called *Nitrosulphates.* These salts, produced by the simultaneous action of nitric oxide and sulphurous anhydride on alkaline liquids, are usually regarded as sulphates in which one atom of oxygen is displaced by 2 atoms of nitrosyl, *e.g.* $K^2SO^3(NO)^2$. A dry mixture of 2 vol. sulphurous anhydride and 4 vol. nitric oxide, though of itself permanent, is gradually absorbed by a strong solution of caustic potash or soda, with formation of a nitrososulphate of alkali-metal. *Nitrososulphate of ammonium* is prepared by passing a current of nitric oxide gas for some hours through a cooled mixture of one measure of concentrated solution of sulphite of ammonium with five or six measures of aqueous ammonia. Beautiful white crystals gradually form, which are to be washed with an ice-cold solution of ammonia, dried in vacuo, and preserved in a well-closed bottle. The *potassium-* and *sodium-salts* may be prepared in a similar manner. They are rather more stable than the ammonium-salts.

Nitrososulphate solutions have a sharp bitter taste; they are neutral to test-paper and do not give any precipitate with chloride of barium. They are permanent only at the freezing point or in presence of an excess of caustic alkali. Their spontaneous decomposition into nitrous oxide and a sulphate varies in its rapidity according to the temperature. Free acids and most metallic salts transform the nitroso-sulphates immediately into sulphuric acid and nitrous oxide gas. A similar decomposition of the salts is effected by contact with spongy platinum, charcoal, oxide of silver, peroxide of manganese, &c.:—

$$K^2SO^3(NO)^2 \quad = \quad K^2SO^4 \quad + \quad N^2O.$$

Dry nitrososulphate of ammonium is decomposed with almost explosive violence when heated to a temperature a little above that of boiling water. (*Odling's Manual of Chemistry*, p. 272.)

**NITROSTILBIC ACID.** $C^{14}H^9(NO^2)O^4$?—An acid formed, together with several other products, by the action of boiling nitric acid on stilbene (*q. v.*). It is a yellowish powder, nearly insoluble in water, but soluble in alcohol, and still more so in ether. (Laurent, Rev. Scient. xvi. 373.)

**NITROSTYROL.** Syn. with Nitrocinnamene. (See Cinnamene, i. 983.)

**NITROSULPHALIC ACID.** Laurent's name for the compound $SO^3(NO^2)H$, which he supposed to constitute the crystals of the sulphuric acid chambers.

**NITROSULPHATES.** Syn. with Nitroso-sulphates.

**NITROSULPHIDES OF IRON.** See Iron (iii. 391).

**NITROSULPHOBENZIDE.** See Sulphobenzide.

**NITROSULPHOBENZIDIC ACID.** Syn. with Nitrophenyl-sulphurous Acid. (See Sulphurous Ethers.)

**NITROSULPHOCYMOLIC ACID.** See Sulphocymolic Acid.

**NITROSULPHONAPHTHALIC ACID.** See Sulphonaphthalic Acid.

**NITROSULPHOTOLUYLIC ACID.** See Sulphotoluylic Acid.

**NITROSULPHOXYLOLIC ACID.** See Sulphoxylolic Acid.

**NITROSYL** or **AZOTYL.** The name of nitric oxide in combination.

**NITROSYL, CHLORIDES OF.** Nitrosyl forms two chlorides, a proto- and a di-chloride.

The *protochloride*, NOCl, also called *Chloronitrous gas*, is produced by the direct combination of chlorine and nitric oxide gases, 1 vol. Cl and 2 vol. NO uniting to form 2 vol. chloride of nitrosyl; it also constitutes the principal product of the latter stage of the decomposition of nitromuriatic acid (p. 112).

Protochloride of nitrosyl is a deep orange-coloured gas. It is condensed by a freezing mixture of ice and salt, into a red fuming liquid, possessing the peculiar smell of nitromuriatic acid. It is decomposed by water into hydrochloric and nitrous acids, and acts in a similar manner on alkaline hydrates, forming a chloride and a nitrite of the alkali-metal:

$$NOCl \; + \; 2KHO \; = \; KCl \; + \; K(NO)O \; + \; H^2O.$$

It is decomposed by mercury, with formation of calomel and liberation of nitric oxide:

$$NOCl \quad + \quad Hhg \quad = \quad HhgCl \quad + \quad NO.$$

It does not act on gold or platinum.

*Dichloride of Nitrosyl*, $NOCl^2$, called by Gay-Lussac, who discovered it, *Chloro-nitric gas*, is obtained by distilling, at a gentle heat in a water-bath, a mixture of 1 pt. of strong nitric acid with about 3 pts. of hydrochloric acid. The products should be passed first through a vessel surrounded with ice, and then through a U-tube immersed in a mixture of ice and salt. In this tube the compound condenses, while free chlorine escapes as gas:

$$HNO^3 + 3HCl = NOCl^2 + 2H^2O + Cl.$$

Dichloride of nitrosyl is a transparent, red, fuming liquid, which may be dried over chloride of calcium. It boils at $-7°$, being converted into a deep lemon-yellow gas or vapour, smelling strongly of nitromuriatic acid. When decomposed by *alkaline hydrates*, it forms a nitrate as well as a nitrite and chloride of the alkali-metal, thus:

$$2NOCl^2 + 6KHO = 4KCl + KNO^2 + KNO^3 + 3H^2O.$$

It reacts in a similar manner with *water*, producing nitrous, nitric and hydrochloric acids. With excess of *mercury* it forms calomel and nitric oxide. It does not act on gold or platinum.

**NITROTARTARIC ACID.** See TARTARIC ACID.

**NITROTHEINE.** Syn. with CHOLESTROPHANE (i. 926).

**NITROTOLUIDINE.** Syn. with NITROBENZYLAMINE. (See BENZYLAMINE, i. 576.)

**NITROTOLUENE** or **NITROTOLUOL.** Syn. with HYDRIDE OF NITROBENZYL. (See BENZYL, HYDRIDE OF, i. 574.)

**NITROTOLUYLAMIDE.** See TOLUYLAMIDE.

**NITROTOLUYLIC ACID.** See TOLUYLIC ACID.

**NITROTYROSINE.** See TYROSINE.

**NITROVALERIANIC ACID.** See VALERIANIC ACID.

**NITROVERATRIC ACID.** See VERATRIC ACID.

**NITROVERATROL.** See VERATROL.

**NITROXAMYLENE.** See AMYLENE (i. 208).

**NITROXAMYLENE, NITROXYSULPHIDE OF.** The name given by Guthrie to the compound $C^{10}H^{18}S(NO^2)^4$, produced by heating disulphochloride of amylene (i. 209) with strong nitric acid. A violent action then takes place, the disulphochloride being partly converted into sulphuric, hydrochloric, and oxalic acid, together with a conjugated sulphuric acid, not yet examined, partly into the compound $C^{10}H^{18}S(NO^2)^4$, which distils over as a heavy green liquid, insoluble in water, and may be obtained pure by washing and drying. It is soluble in alcohol and ether, and appears to be very easily decomposed by sulphide of ammonium. (Guthrie, Chem. Soc. Qu. J. xiv. 138.)

**NITROXIN** or **NITROXYL.** Syn. with NITRYL.

**NITROXYBENZOIC ACID.** See OXYBENZOIC ACID.

**NITROXYLENE** or **NITROXYLOL.** See XYLENE.

**NITROXYL-PIPERIDINE.** The name given by Wertheim to the compound, $C^5H^{10}(NO)N$, more properly called *Nitroso-piperidine*. (See PIPERIDINE.)

**NITROXYNAPHTHALIC ACID.** $C^{10}H^8NO^3 = C^{10}H^7(NO^2)O$ ? (Dusart, Compt. rend. lii. 1183; Rép. Chim. pure, 1861, p. 315; Jahresb. 1861, p. 644.)—An acid produced by the oxidation of nitronaphthalene. When a mixture of 1 pt. nitronaphthalene, 1 pt. caustic potash, and 2 pts. slaked lime is heated to 140° in a tubulated retort, through which a current of air or oxygen is slowly passed, the gas is absorbed, the mixture turns yellow, and the oxidation is nearly completed in ten or twelve hours. Water extracts from the product a reddish-yellow potassium-salt possessing great colouring power, and acids added to the solution throw down a thick yellow magma of nitroxynaphthalic acid, which may be purified by washing with water.

Nitroxynaphthalic acid dissolves easily in *water*, *alcohol*, *wood-spirit*, and *acetic acid*, and crystallises from the latter on cooling in needle-shaped crystals of a fine golden yellow colour. It has a cooling taste with bitter after-taste. It melts at about 100°, and is not volatile. It is a weak acid, forming with the *alkalis*, strongly coloured, very soluble, crystallisable salts, the solutions of which form coloured precipitates with metallic salts. It unites with acid *sulphate of potassium*, forming a colourless salt.

Dusart assigns to nitroxynaphthalic acid the formula $C^{20}H^7(NO^4)O.HO$, and to its

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salts the formula $C^{20}H^{7}(NO^{4})O.MO$, that is to say he regards the acid as differing from nitronaphthalene by the addition of 1 at. water ($HO$), and 1 at. $O$, or by 1 at. $HO^{2}$. As such a constitution is contrary to all analogy, Wurtz (Rép. Chim. pure, 1861, p. 316) suggests that the acid may be formed from nitronaphthalene, either by addition of 2 at. HO, making the formula $C^{20}H^{9}(NO^{4})O^{2}$ or $C^{10}H^{9}(NO^{2})O$, or else by addition of 2 at. $HO^{2}$ or HO to 2 at. nitronaphthalene, which would give the formula $C^{20}H^{16}N^{2}O^{6} = C^{20}H^{16}(NO^{2})^{2}O^{2}$.

Nitroxynaphthalic acid becomes heated in contact with *sulphuric acid*, and eliminates sulphurous anhydride. It is strongly attacked by *nitric acid*, yielding oxalic acid and a resin which by prolonged action is converted into phthalic acid. By *reducing agents* it is converted into oxynaphthylamine, a weak base to which Dusart assigns the formula $C^{20}H^{10}NO^{2}$. It is more probably either $C^{10}H^{11}NO^{2}$ or $C^{20}H^{20}N^{2}O^{2}$.

**NITRUM.** This name is or has been applied to several salts of nitric acid and products derived from them, *e.g.*: *Nitrum antimoniatum:* an obsolete pharmaceutical preparation consisting chiefly of nitrite of potassium mixed with nitrate and sulphate of potassium, obtained as a bye-product in the preparation of washed oxide of antimony (*antimonium diaphoreticum ablutum*), by igniting sulphide of antimony with saltpetre and washing the product with water.—*Nitrum cubicum:* nitrate of sodium.—*Nitrum fixum:* nitrate of potassium; also carbonate of potassium obtained by deflagrating saltpetre with charcoal.—*Nitrum flammans:* nitrate of ammonium.—*Nitrum tabulatum* or *Sal prunellæ:* fused saltpetre (p. 101).

**NITRYL.** Nitric peroxide in combination (see page 77).

**NOMENCLATURE.** Chemical nomenclature is the spoken language of chemistry, as the Symbolic NOTATION is the written language of the science. Being thus at once the product and the instrument of thought upon chemical subjects, it has necessarily, at every period in the history of the science, reflected the general intellectual character of the time, as well as the stage of development which chemistry had reached. Thus the early and deeply rooted belief that the heavenly bodies exercised a direct influence on all terrestrial affairs, gave rise, among the early cultivators of physical science, to the idea that they severally determined the characters and properties of the different metals; and this idea recorded itself in the language of chemistry by such names as *Sol* for gold, *Luna* or *Diana* for silver, *Mercury* for quicksilver, *Jupiter* for tin, *Mars* for iron, *Venus* for copper, and *Saturn* for lead. Traces of this nomenclature still remain in expressions not yet gone quite out of use; as Lunar caustic, *arbor Dianæ*, Martial pyrites, tincture of Mars, Saturnine poisoning, and the like, to say nothing of mercury, which is still universally employed. The language of the alchemists was made up in great part of names involving far-fetched comparisons, indicating the mystical habits of thought of those who invented and employed them, so that it is now next to impossible to say upon what principles it was founded—if, indeed, it was based upon any general principles at all—or what ideas it was meant to convey. In the language of Lavoisier, speaking of the alchemists—"Il leur aurait été difficile de transmettre à leurs lecteurs ce qu'ils n'avaient pas eux-mêmes, des idées justes et vraies. De plus leur objet n'était pas toujours de se faire entendre. Ils se servaient d'un langage énigmatique qui leur était particulier, qui, le plus souvent, présentait un sens pour les adeptes, un autre sens pour le vulgaire, et qui n'avait rien d'exact et de clair ni pour les uns, ni pour les autres. C'est ainsi que l'huile, le mercure, l'eau elle-même des philosophes n'étaient ni l'huile, ni le mercure, ni l'eau dans le sens que nous y attachons. L'*homo galeatus*, l'homme armé, désignait une cucurbite garnie de son chapiteau; la tête de mort, un chapiteau d'alembic; le pélican exprimait un vaisseau distillatoire; le *caput mortuum*, la terre damnée, signifiait le résidu d'une distillation." At a later period, ideas of a more material order inspired the language of our science, and slight resemblances in some external character between certain chemical products and common articles of household life, gave rise to such names as *oil* of vitriol, *oil* of tartar by deliquescence, *cream* of tartar, *milk* of lime, *butter* of antimony, *sugar* of lead, *liver* of sulphur;—names which surely justified Dumas in saying "Les chimistes semblaient avoir emprunté le langage des cuisinières." But the inappropriate character of the names of individual substances was not the only defect of chemical nomenclature in early times: another great fault was the multiplicity of names borne by a single substance. Thus, for example, the body now known as sulphate of potassium was called *vitriol of potash*, *vitriolised tartar*, *vitriolised nitre*, *sal de duobus*, *arcanum duplicatum*, *sal duplicatum*, *panacea duplicata*, *sal polychrestum Glauberi*; and carbonate of potassium was *fixed salt of tartar*, *fixed vegetable alkali*, *aërated fixed vegetable alkali*, *chalky tartar* (tartre crayeux), *mephitic tartar*, *nitrum fixum per se*, *Alkahest of Vanhelmont*, *alcali extemporaneum*, &c.

According to Lavoisier, the merit of having made the first attempt towards the

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introduction of a nomenclature based upon truly chemical principles, is chiefly due to **Macquer** and **Baumé**: "C'est à eux qu'on doit principalement d'avoir désigné les sels métalliques par le nom de l'acide et du métal qui entrent dans leur composition; d'avoir classé sous le nom de *vitriols* tous les sels résultants de la dissolution d'une substance métallique dans l'acide vitriolique; sous le nom de *nitres* tous les sels dans lesquels entre l'acide nitreux" [nitric acid]. A further advance towards a systematic nomenclature was made by **Bergman** in his *Sciagraphia regni mineralis*, first published in the Upsal Transactions, and issued separately in 1782 (the edition that has been consulted is dated London, 1783), and in his *Thoughts on a Natural System of Fossils* published at about the same time. This work has been consulted in "Essays Physical and Chemical, by Sir Torbern Bergman," Edinb. 1791. In the former work, names made up of a noun-substantive to indicate the base, and an adjective denoting the acid, are given to the salts of the alkalis, earths, and metals. The following is a specimen of this nomenclature:—

| Modern names. | Bergman's names. |
|---|---|
| Sulphate of Potassium | *Alkali vegetabile vitriolatum.* |
| Nitrate ,, | *Alkali vegetabile nitratum.* |
| Chloride ,, | *Alkali vegetabile salitum.* |
| Carbonate ,, | *Alkali vegetabile aëratum.* |
| Sulphate of Sodium | *Alkali minerale vitriolatum.* |
| Nitrate ,, | *Alkali minerale nitratum.* |
| Chloride ,, | *Alkali minerale salitum.* |
| Carbonate ,, | *Alkali minerale aëratum.* |

The earths being distinguished as *terra ponderosa*, *calx*, *magnesia*, *argilla*, and *terra silicea*, the names of their salts were formed in the same way as those of the salts of the alkalis: as, *terra ponderosa vitriolata*, *calx fluorata*, *magnesia aërata*. The metallic salts also were named in the same manner, *e.g. ferrum vitriolatum*, *ferrum aëratum*, *ferrum nitratum*, *ferrum salitum*, *zincum vitriolatum*, &c. In the second of the works mentioned above, the latter part of which specially treats "Of giving Names to Fossils," **Bergman** suggested a still more systematic nomenclature. In the first place, he proposed to designate all metals by names ending in *-um*, and accordingly replaced the *platina* of the Spaniards by *platinum*. The acids he denoted by adjectival substantives, as follows:—*vitriolicum* (sulphuric), *sulphureum* (sulphurous), *nitrosum* (nitric), *nitreum* (nitrous), *muriaticum*, *regalinum*, *fluoratum*, *arsenicale*, *boracinum*, *saccharinum*, *oxalinum*, *tartarum*, *phosphoreum*, *formicale*, *aëreum*, &c.—*acidum* being in each case understood. By adding to the names of the acids adjectives formed from those of the several bases, he obtained names for the neutral salts; as, for example, *vitriolicum potassinatum*, *vitriolicum natratum*, *muriaticum ammoniacum*, *nitrosum barytatum*, *muriaticum barytatum*, *nitrosum argentatum*, *arsenicale cobaltatum*. He even went so far as to point out how salts formed by the combination of the same acid and base in various proportions might be distinguished: thus—"Tartar, with an excess of acid, can be defined by a combination of its generic name with the genitive of its base, as *tartareum potassini*; but, when perfectly saturated, may be called *tartareum potassinatum*. In like manner we shall have *oxalinum potassini*, but, when exactly saturated, it will be *oxalinum potassinatum*; *vitriolicum natri*, and *vitriolicum natratum*; *natrum boracini* [*boracinum natri?*], and *boracinum natratum*; and so on of others." We have in this passage probably the first instance of the systematic employment of the method which has been used to so great an extent, and with so much advantage in modern chemical nomenclature—that, namely, of employing definite inflections or changes of termination to express definite differences of composition.

About the same time that these reforms were proposed by **Bergman**, a similar attempt was made in France by **Guyton de Morveau**. The suggestions of the French chemist were first published in the *Journal de Physique* for May, 1782, and were known to **Bergman** when he published his later system: for he expressly states that he adopts the terms *barites* in place of *terra ponderosa* from de Morveau, but he at the same time asserts, by implication, the independent character of his own nomenclature, by expressing his satisfaction at the agreement he finds between many of de Morveau's proposed reforms and his own. The respectful terms in which each author speaks of the other, forbid us to think that either was in any degree chargeable with plagiarism; but the following specimen of **de Morveau's** nomenclature (quoted by **Dumas** in his *Leçons de Philosophie Chimique*, p. 228), will show that it closely resembled Bergman's, not only in the principles of its formation and its range of application, but also in several of the individual names adopted.

*Specimen of Guyton de Morveau's system of Chemical Nomenclature.*

| Acides. | Sels. | Bases. |
|---|---|---|
| Vitriolique | Vitriols | Phlogistique |
| Nitreux | Nitres | Calce |
| Arsénical | Arséniates | Baryte |
| Boracin | Boraxs | Or |
| Fluorique | Fluors | Argent |
| Citronien | Citrates | Platine |
| Oxalique | Oxaltes | Mercure |
| Sébacé | Sébates | Cuivre |
| | | Esprit de vin. |

Although de Morveau's suggestions do not appear to have produced any immediate effect of importance, the attention which he succeeded in calling to the subject resulted soon afterwards in the publication of a much more complete and more successful plan of reform. This system of nomenclature—the joint production of Lavoisier, de Morveau, Berthollet, and Fourcroy—was published in 1787, under the title "*Méthode de Nomenclature Chimique, proposée par MM. de Morveau, Lavoisier, Bertholet, et de Fourcroy,*" (Paris, 1787, 8vo.), and still continues the foundation of the language which, with many variations in minor points, is employed by all chemists at the present day. It was based upon the fundamental propositions that all substances which cannot be decomposed must be regarded, provisionally at least, as simple; and that the names of compound bodies ought to indicate the simple bodies which they contain, and also, as far as possible, their relative proportions. Thus the compounds of *oxigène* were subdivided into *oxides* and *acides*, and these latter were again distinguished by specific names ending in *-eux* or *-ique* respectively, according as they contained less or more oxygen: for example, *oxide d'arsenic, acide arsénique, oxide nitreux, acide nitreux, acide nitrique; acide sulfureux, acide sulfurique.* When, however, several compounds of the same elements in different proportions were known, it was found impracticable to carry out the second fundamental rule to its full extent, and in such cases, as for instance in the case of the organic acids, arbitrary names were adopted, which recalled the derivation of the substances to which they were applied, and were similar in form to the names formed more strictly according to rule. Thus, for example, came such names as *acide succinique, acide malique, acide tartareux,* &c. The very important rule according to which the names of metallic and other salts are formed from the names of the corresponding acids—the former being made to end in *-ite* or *-ate* respectively when the latter ended in *-eux* or *-ique*—was also now introduced for the first time. The nomenclature of this class of bodies thus became very nearly what it is at present, as will appear from a few examples:—*sulfate d'alumine,* or *sulfate alumineux; nitrite d'ammoniaque,* or *nitrite ammoniacal; nitrate d'ammoniaque* or *nitrate ammoniacal; carbonate barytique,* or *carbonate de baryte; phosphate de soude,* &c. &c.

The mineral acids, oxides, and neutral salts being almost the only chemical substances which had been much studied at the time of which we are speaking, it is no reproach to the nomenclature of Lavoisier and de Morveau to say that in its original form it was not applicable to many compound bodies besides these; but the fact that so much of their system is still retained, and that our present nomenclature has resulted from it by a process of development, rather than of organic change, is a striking proof how well they succeeded in their professed object of devising "une méthode de nommer, plutôt qu'une nomenclature."

It is obvious from what has been said that Lavoisier's nomenclature was an embodiment of the antiphlogistic doctrines in chemistry, and accordingly we find that the history of its spread and adoption is, in the main, the history of the advance of these doctrines. It naturally came into general use earlier in France than elsewhere, but according to Kopp (*Geschichte,* ii. 418), it was adopted by Black and other leading English chemists almost from the first.[*] The *Système de Nomenclature* was translated into English by Pearson, the translation reaching a second edition in 1799. In 1802 Chenevix published a work, ably advocating its adoption, and one of the earliest important improvements which it received was due to Dr. Thomas Thomson, who in 1804 introduced the terms *protoxide, deutoxide, peroxide,* &c., to distinguish the different degrees of oxidation of the same metal. The new nomenclature was translated into German by Girrtanner, in 1791, under the title *Neue chemische Nomenclatur für*

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[*] This statement cannot be more than partially true in so far as it relates to Black; for according to Robison, "He disliked the avowed principle of the nomenclature, thinking it more likely to corrupt science than to promote it; and he began to write some observations upon it, but he soon desisted." (Black's *Lectures on the Elements of Chemistry*, vol. ii. p. 218.)

*die deutsche Sprache* (Berlin), but its general adoption in Germany was due in great measure to Gren and to Gilbert, the editor of the *Annalen der Physik*, a journal which was the forerunner, from 1799 to 1824, of the present "Poggendorff's Annalen der Physik und Chemie." In 1795 it was translated into Swedish by Ekeberg, and was employed by Berzelius in his earliest memoirs.

In 1814, a nomenclature based upon similar principles, but as was supposed by its author more in harmony with the genius of the languages of Northern Europe, was proposed by Oersted of Copenhagen. The following are a few examples of this nomenclature: Eld, oxygen (from Ild = fire, *Danish*); Eldluft, oxygen gas; elden, to oxidise; Brint, hydrogen (from brennen = to burn, *Germ.*); Æsch, alkali; æschig, alkaline; Tanæsk, potash; Natersæk, soda; Svafvelbrintadt Svafveltanæsk, sulphydrate of potassium.

The spread of the new nomenclature was not however altogether unopposed even by chemists who accepted the most important doctrines of the antiphlogistic school. Sir Humphry Davy in particular objected to it, on the ground that it was based upon theoretical views of the composition of bodies. While admitting that the principle of regarding undecomposed bodies as simple, was "logical and truly philosophical," he contended that this principle could not be safely taken as the basis of a nomenclature, until all the elements were certainly known; and hence he preferred such names as *metals, earths, alkalis* (which merely class together as similar the bodies to which they are applied), to names like *oxides, sulphurets, muriates* (which involve a theoretical explanation of the similarity of the bodies denoted by them). In applying these views to the nomenclature of individual substances, Davy endeavoured "to signify the analogies of substances by some common sign affixed to the beginning or termination of the word." Thus, as the metals had been distinguished by a termination in *um* as *aurum*, "so," he said, "their calciform or oxidated state might have been denoted by a termination in *a*, as *aura*," a rule already followed in the Latin nomenclature of the alkalis and earths, which Davy's own experiments had proved to belong to the class of oxides. Similarly he proposed to denote the chlorides containing one proportion of chlorine by names ending in *-ane*, and those containing two and three proportions respectively, by names in *-ana*, and in *-anée;* for the iodides he proposed names in *-ame*, and *-ama;* for the fluorides, names in *-ale*, and *-ala*. According to this system the oxide, fluoride, iodide and chloride of lead were called respectively *plumba, plumbala, plumbama*, and *plumbana*, and the corresponding compounds of other elements received names similar in form. When he proposed this nomenclature, Davy seems to have overlooked the fact that the statement that any two bodies are analogous, is just as truly, and usually to about the same extent, an *expression of opinion* respecting them, as it is to say that they contain some particular element in common. The only relic of this system which we remember meeting with in the current literature of chemistry is Azotan, which is entered in the *Handwörterbuch der Chemie* (2nd edit.) as "a little used name for chloride of nitrogen."

Several other attempts, not more successful than that of Davy, have been made to substitute some entirely different method of nomenclature for that proposed by Lavoisier and his colleagues, but it would offer no particular interest to examine them here. References to works, where particulars may be found relative to some of these attempts, are given at the end of this article.

It is also needless to particularise all the modifications, by the gradual introduction of which the Lavoisierian nomenclature has developed into the language employed by chemists at the present day. The most important of these changes have had for their object, either the substitution of names in accordance with modern views of the nature of certain substances for earlier names which were in opposition thereto (as of *chlorine* and *hydrochloric acid* for *oxymuriatic acid* and *muriatic acid* respectively); the more exact statement of the quantitative composition of compounds (as for instance the employment of the prefixes *per-*, *hypo-*, &c., in addition to the terminations *-ic* and *-ous*, *-ate* and *-ite*, to distinguish the various classes of oxygen-salts formed by the same element, and the use of numerical prefixes, such as *di-*, *tri-*, *sesqui-*, for analogous purposes); or, lastly, the introduction of greater uniformity in the methods of naming analogous compounds (as the employment of the termination *-ide* in forming the names of the binary compounds of all the elements, that is to say, the substitution of such names as *sulphide*, *hydride*, &c., for *sulphuret, hyduret*, &c.; the extension of the use of the terminations *-ic* and *-ous* to metallic salts, such as *mercuric* and *mercurous* chloride, *ferric* and *ferrous* sulphate, &c.; and the substitution of the names of the alkali-metals and alkaline-earth metals for those of their oxides in the nomenclature of the corresponding oxygen-salts, *e.g.*, *carbonate of sodium*, *sulphate of barium*, &c., for *carbonate of soda*, *sulphate of baryta*, &c., so as to bring the names of these bodies into uniformity with those of the salts of the heavy metals, *sulphate of copper* for example[*]).

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[*] The names sulfate de *soude*, sulfate de *baryte*, sulfate de *cuivre*, &c., were originally strictly analogous to each other, soda, baryta and copper being all of them regarded as simple bodies; but

In stating the rules which are now most generally adopted in forming the names of chemical substances, it will be convenient to retain the old distinction between inorganic and organic compounds, the nomenclature of the former class being, as we have already stated, for the most part a mere extension of that of Lavoisier and his colleagues; while, among the latter class, the large number of bodies composed of the same elements has necessitated the at least partial adoption of other principles of nomenclature.

### NOMENCLATURE OF INORGANIC BODIES.

*Names of the Elements.*—No uniform principle has been followed in the nomenclature of the elementary bodies. Those which have been long known, have been allowed to retain, either entirely unaltered, or with slight modifications, the names which belonged to them in common language; as iron, sulphur, tin, zinc, carbon, &c. Of elements discovered in recent times, those of which compounds were previously known have generally received names derived from those of their best known compounds, as potassium, sodium, aluminium, magnesium, silicium. Elements whose discovery belongs more completely to modern times have been named in very various ways; sometimes from the name of the place where the substance which first yielded the element was originally found, as strontium from Strontian, and yttrium, terbium and erbium from Ytterby; sometimes from some characteristic property of the element itself or of its compounds, as iodine, bromine, rhodium, osmium, chromium; sometimes from the circumstances which led to the discovery of the element, as cæsium, rubidium, thallium, indium, all of which names refer to the colour of the spectroscopic lines by means of which the respective metals were detected; sometimes a salient chemical or physical property has determined the choice of the name, as in the cases of oxygen, and chlorine. Many names of elements commemorate personages of classical mythology, as palladium, niobium, titanium, selenium, tellurium, uranium; while two, thorium and vanadium, perform the same office for Scandinavian deities.

But notwithstanding this great variety in the sources from which the names of the elementary bodies are derived, these names yet exhibit a certain amount of regularity in regard to their forms: thus, the majority of the metals, including all those discovered in recent times, have names ending in *-um*, and this termination is confined exclusively to well characterised metals and to selenium, tellurium, and silicium, bodies which lie nearly upon the border-line between metals and metalloïds; again, the names of the halogens fluorine, chlorine, bromine, and iodine all end in *-ine*, and the names of another group of somewhat analogous elements, boron, carbon, and silicon * (or silicium), have the common termination *-on*.

*Names of Inorganic Compounds.*—The simplest compounds of the elementary bodies are denoted by names ending in *-ide*; thus:—

The simplest compounds of chlorine are called chlorides.
„ „ bromine „ „ bromides.
„ „ hydrogen „ „ hydrides.
„ „ oxygen „ „ oxides.
„ „ sulphur „ „ sulphides.
„ „ nitrogen „ „ nitrides.
„ „ phosphorus „ „ phosphides.
„ „ carbon „ „ carbides.
&c. &c.

These names may be considered as names of *genera:* in order to denote individual compounds we require to add to them *specific* distinctions indicating the second element which each particular compound contains. The specific name of a compound body is formed from its generic name by prefixing an adjective, generally ending in *-ic*, or by adding thereto the name of its second elementary constituent preceded by *of*. Thus

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when the alkalis and earths had been proved by Davy to be metallic oxides, the nomenclature of their salts ceased to be in exact accordance with that of the corresponding salts of the heavy metals. The clumsy remedy for this state of things which consisted in designating the latter class of salts by names like sulphate of *oxide of copper*, sulphate of *protoxide of iron*, sulphate of *sesquioxide of iron*, &c., would assuredly never have been adopted by Lavoisier. It is plain from many passages in his writings (see, for instance, his *Traité élémentoire de Chimie*, vol. i. pp. 174, 176-180, and 195), that he was fully aware of the important differences exhibited by metals on the one hand, and by metallic oxides or alkalis and alkaline-earths on the other hand, in the phenomena which accompany their conversion into salts, and that he even regarded these phenomena as indicating that the alkaline-earths were in reality metallic oxides. He nevertheless did not venture to introduce into the names of the salts of these substances, the names of the metals which he supposed them to contain, inasmuch as the existence of these metals had not yet been experimentally demonstrated; but *had* these metals been known, it is quite certain that their names, and not those of their oxides, would have been selected by him to form the basis of the nomenclature of the corresponding salts. See also Chenevix, *Remarks upon Chemical Nomenclature* (Lond. 1802), pp. 30, 79.

* The name *Gropbon* (*q. v.*) is formed upon the analogy of these.

the compounds of chlorine with hydrogen, potassium and silver, respectively, are called hydric chloride or chloride of hydrogen, potassic chloride or chloride of potassium, and argentic chloride or chloride of silver. When the relative electro-chemical characters of the constituents of a binary-compound are well marked, the most electro-negative of the two is always taken as the one which shall supply the generic name, while the specific designation is derived from the more electro-positive constituent, as in the foregoing examples. When there is no very distinct difference in the positions of the two constituents in the electro-chemical series, the generic or specific name may be formed from either of them indifferently: thus, we may say either carbide of hydrogen or hydride of carbon.

If the same two elements combine in more than one proportion, the compound into which they enter in the ratio directly indicated by their respective combining capacities (CLASSIFICATION, i. 1011) is generally named in accordance with the above rules; the modes of distinguishing compounds in other proportions will be seen by the following examples:—

$H^2O$ = hydric oxide, or oxide of hydrogen,
$H^2O^2$ = hydric dioxide, or dioxide of hydrogen;
$CuCl^2$ = cupric chloride, or chloride of copper,
$Cu^2Cl^2$ = cuprous chloride, or dicupric chloride, or (if regarded as $CuCl = \frac{Cu^2Cl^2}{2}$) cupric hemichloride, or hemichloride of copper, or subchloride of copper;
$CuO$ = cupric oxide, or oxide of copper,
$Cu^2O$ = cuprous oxide, or dicupric oxide, &c.;
$FeO$ = ferrous oxide, or protoxide of iron,
$Fe^2O^3$ = ferric oxide, or sesquioxide of iron;
$MnO$ = manganous oxide, or protoxide of manganese,
$Mn^2O^3$ = manganic oxide, or sesquioxide of manganese,
$Mn^3O^4$ = manganoso-manganic oxide,
$MnO^2$ = manganic dioxide, or dioxide of manganese, or manganic peroxide, or peroxide of manganese.

It will be seen that in the case of iron and manganese, the simple names *ferric oxide* and *manganic oxide* are not given to compounds whose composition bears the most direct relation to the atomicity of these metals, and many other instances of the same kind might be adduced. The reason of this is that the nomenclature of these compounds was fixed long before the rules of atomicity had been discovered; the terms ferrous and ferric, manganous and manganic, and the like, having been employed at first merely to denote two distinct series of compounds formed by the same elements in different proportions, but without any reference to the absolute proportion of the elements in the compounds of either series.

The nomenclature of chemistry still bears traces of the time when the combinations of oxygen were considered as altogether transcending in importance those of any other element. Accordingly the terms *protoxide* and *sesquioxide* having been introduced to denote oxides whose atomic composition was expressed by the ratios 1 : 1 and 2 : 3 respectively, the analogous terms *protochloride* and *sesquichloride* are applied to the corresponding chlorine-compounds, although in their case the above ratios become 1 : 2 and 2 : 6, *e.g.* $FeCl^2$ = protochloride of iron, $Fe^2Cl^6$ = sesquichloride of iron. Sometimes, however, the term protoxide is used to denote the *first*, or lowest, oxide of a metal whatever its atomic composition may be; thus, for instance, cuprous oxide, $Cu^2O$, is sometimes called protoxide of copper, especially in the writings of French chemists, and the other compounds of the metal receive corresponding names; *e.g.* cupric oxide, $CuO$, becomes deutoxide of copper. Such names as these are not however to be recommended, since the discovery of a new oxide of any metal might at any time throw the nomenclature of its compounds into confusion.

Formerly a distinction was made, at least by some chemists, between the Greek and Latin numerals when used as prefixes, the former being employed to denote sub-multiples and the latter multiples of the quantity of the electronegative element contained in the compound whose atomic ratio was 1 : 1. Thus, cuprous oxide, $Cu^2O$, was called *dioxide of copper*, and manganic peroxide, $MnO^2$, was called *binoxide of manganese*. Such prefixes, whether derived from the Greek or Latin, are employed in this work only in the sense of multiples of those constituents to whose names they are attached, thus, hydric dioxide, $H^2O^2$, is an oxide containing twice as much oxygen as hydric

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oxide, $H^2O$; but dicupric oxide, $Cu^2O$, is an oxide containing twice as much copper as cupric oxide, $CuO$. Terms derived from either language may sometimes be used indiscriminately, but in general the preference is given to the Greek prefixes *di-*, *tri-*, *tetr-*, &c.

The restriction of the terms *suboxide* and *peroxide* to oxides whose composition did not correspond to that of a series of salts has now become nearly obsolete.

Those oxides, which by reacting with the basylous oxides are capable of producing salts, are commonly called anhydrides (*quasi* anhydrous acids):—for instance, $SO^2$ = *sulphurous anhydride*, $SO^3$ = *sulphuric anhydride*, $Cl^2O$ = *hypochlorous anhydride*, $Cl^2O^3$ = *chlorous anhydride*, $Cl^2O^5$ = *chloric anhydride*, $Cl^2O^7$ = *perchloric anhydride*, &c.; and Gerhardt proposed to extend the same principle of nomenclature to the corresponding compounds of other elements: thus he called $P^2O^5$ *phosphoric anhydride*, and $P^2S^5$ and $PCl^5$ *phosphoric sulphanhydride* and *phosphoric chloranhydride* respectively. Such names as these last have not been extensively adopted, and it would probably be a greater advantage to get rid of the term anhydride altogether than to generalise its use in this way. The longest series of oxides may be easily named in the manner indicated above (p. 123) without employing the word anhydride at all: as $Cl^2O$, chloric oxide; $Cl^2O^2$, chloric dioxide; $Cl^2O^3$, chloric trioxide; $Cl^2O^4$, chloric tetroxide; $Cl^2O^5$, chloric pentoxide, &c. Names like *perchloric oxide* for $Cl^2O^4$ and *pernitric oxide* for $N^2O^4$ are improper; if the prefix *per-* is preferred to the more definite numerical prefix *tetr-*, the compounds should be called chloric peroxide and nitric peroxide respectively; and so for other similar bodies.

As well as the strictly systematic names which we have hitherto been discussing, many binary compounds possess other names which must be regarded as, to some extent, exceptions to the general rules of nomenclature. This is the case particularly with the compounds of hydrogen: thus hydric fluoride, chloride, bromide, iodide, and sulphide are also called hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, and sulphydric acid respectively. Names such as water and ammonia, which have no reference to chemical composition, we have not now to consider.

As has been pointed out in previous articles (CLASSIFICATION, i. 1015; EQUIVALENTS, ii. 492; FORMULÆ, ii. 696), the simplest compounds are those in which the combining capacities of the elements are generally most distinctly manifested, and consequently such compounds serve as standards of comparison or types for others of much more complex composition. In a rational nomenclature, therefore, the name of each compound would, like its rational formula, express the relation in which it stands to some particular standard or typical compound. Accordingly, when the nomenclature of the primary types *chloride*, *oxide*, *nitride*, &c, is given, the nomenclature of all their immediate derivatives is easily obtained. The examples already given will suffice to illustrate this in the simplest cases; the polyatomic elements however frequently form compounds referable to multiple or mixed types, the nomenclature of which requires a little further explanation. It will be sufficient however to give the names of the most important multiple and mixed types, with a few examples of the nomenclature of individual compounds.

The names of the multiple types are formed from those of the simple types by prefixing the syllables *di-*, *tri-*, *tetr-*, &c.: thus, the simple types chloride $HCl$, oxide $H^2O$, and nitride (or amide) $H^3N$, give the multiple types dichloride $H^2Cl^2$, trichloride $H^3Cl^3$, &c., dioxide $H^4O^2$, trioxide $H^6O^3$, &c., dinitride (or diamide) $H^6N^2$, trinitride (or triamide) $H^9N^3$, &c. No very fixed system has yet been adopted for the nomenclature of the mixed types, but they may be very simply named and with scarcely any departure from established usage, as follows: $\left.\begin{matrix}HCl\\HBr\end{matrix}\right\}$ = chloro-bromide, $\left.\begin{matrix}H^2Cl^2\\HBr\end{matrix}\right\}$ = dichloro-bromide, $\left.\begin{matrix}HCl\\H^2Br^2\end{matrix}\right\}$ = chloro-dibromide, &c.; $\left.\begin{matrix}HCl\\H^2O\end{matrix}\right\}$ = oxi-chloride, $\left.\begin{matrix}H^2Cl^2\\H^2O\end{matrix}\right\}$ = oxi-dichloride, $\left.\begin{matrix}HCl\\H^4O^2\end{matrix}\right\}$ = dioxi-chloride, $\left.\begin{matrix}H^2Cl^2\\H^6O^3\end{matrix}\right\}$ = trioxi-dichloride, &c.; $\left.\begin{matrix}HCl\\H^3N\end{matrix}\right\}$ = chloro-nitride, $\left.\begin{matrix}H^2Cl^2\\H^3N\end{matrix}\right\}$ = dichloro-nitride, $\left.\begin{matrix}HCl\\H^6N^2\end{matrix}\right\}$ = chloro-dinitride, &c.; $\left.\begin{matrix}H^2O\\H^3N\end{matrix}\right\}$ = oxi-nitride, $\left.\begin{matrix}H^4O^2\\H^3N\end{matrix}\right\}$ = dioxi-nitride, $\left.\begin{matrix}H^2O\\H^6N^2\end{matrix}\right\}$ = oxi-dinitride, &c.; $\left.\begin{matrix}HCl\\H^2O\\H^3N\end{matrix}\right\}$ = oxi-chloro-nitride, &c. The name *hydoramide* or *hydoramine* has been suggested by Kekulé for the mixed type $\left.\begin{matrix}H^2O\\H^3N\end{matrix}\right\}$, and has been employed in several places in this work.

From the names of types, the names of particular compounds are obtained by prefixing to them adjectives which express the nature of the element by which the hydrogen of the type is replaced and the number of atoms of it contained in one molecule of the compound. Examples: $PtCl^2$ = platinic dichloride, $Pb^2O^3$ = diplumbic trioxide, $Pb^3O^4$ = triplumbic tetroxide, $\left.\begin{matrix}Pb^2\\H^2\end{matrix}\right\}O^3$ = diplumbo-dihydric trioxide, $\left.\begin{matrix}Pb^3\\H^2\end{matrix}\right\}O^4$ = triplumbo-dihydric tetroxide, $Bi\left\{\begin{matrix}Cl\\O\end{matrix}\right.$ = bismuthic oxi-chloride, $Pb^2\left\{\begin{matrix}Cl^2\\O\end{matrix}\right.$ = diplumbicoxi-dichloride, $Pb^3\left\{\begin{matrix}Cl^2\\O^2\end{matrix}\right.$ = triplumbic dioxi-dichloride, $Hg^3\left\{\begin{matrix}Cl^2\\O^2\end{matrix}\right.$ = trimercuric dioxi-dichloride, $\left.\begin{matrix}HgCl\\H^2N\end{matrix}\right\}$ = mercuro (or hydargyro-) dihydric chloro-nitride, $\left.\begin{matrix}Hg^4O^3\\H^4N^2\end{matrix}\right\}$ = tetramercuro-tetrahydric trioxi-dinitride, $\begin{matrix}Hg^4\\H^4\end{matrix}\left\{\begin{matrix}Cl^2\\O^2\\N^2\end{matrix}\right.$ = tetramercuro-tetrahydric dioxi-dichloro-dinitride.

When we are able to assume that the combining capacity of an element is known, there is no need to express this in the names of its compounds, and in that case names formed as above often admit of considerable simplification. Thus it is sufficient to call $BaCl^2$ *barytic chloride*, instead of barytic dichloride; $BaH^2O^2$ *baryto-hydric oxide*, instead of baryto-dihydric dioxide; $BiCl^3$ *bismuthic chloride*, instead of bismuthic trichloride, &c. A further simplification of many of the above names is effected by using the term hydrate for derivatives of the type $H^2O$ and its multiples in which the hydrogen is only partially replaced by other elements, and the term amine or amide for compounds derived by similar partial replacement from the type $H^3N$ and its multiples. For instance KHO may be called *potassic hydrate* instead of potassio-hydric oxide; $BaH^2O^2$ may be called *barytic hydrate* instead of baryto-hydric oxide or baryto-dihydric dioxide; $BiH^3O^3$ may be called *bismuthic hydrate* instead of bismutho-trihydric trioxide; $Fe^2H^6O^6$ may be called *ferric hydrate* instead of diferrico-hexhydric hexoxide, &c. Similarly, $KH^2N$ may be called *potassamine*, instead of potassio-dihydric nitride; $K^2HN$ may be called *dipotassamine*, instead of dipotassio-hydric nitride, &c. The use of the terms phosphamine, arsenamine, and stibamine for the respective compounds $H^3P$, $H^3As$, and $H^3Sb$ is improper, inasmuch as the termination *-amine* (derived from ammonia) ought to be reserved for the compounds of nitrogen, the characteristic element of ammonia; they moreover completely violate the analogy of such names as those last spoken of, for if potassamine and mercuramine are compounds derived from ammonia by the substitution of potassium and mercury for hydrogen, phosphamine, arsenamine and stibamine ought to be bodies similarly derived by the substitution of phosphorus, arsenic and antimony for hydrogen. $H^3P$, $H^3As$, and $H^3Sb$ ought to be called either *hydric phosphide*, *hydric arsenide*, and *hydric stibide*, or *phosphine*, *arsine*, and *stibine*.

The rules followed for the nomenclature of the *oxygen-salts* are essentially the same as for the compounds we have been hitherto considering, except that instead of the termination *-ide* we have the terminations *-ate* and *-ite*. When an element forms only one class of salts, the name of the class is formed from that of the element itself by means of the termination *-ate*. When an element forms two classes of salts the generic name of those which contain most oxygen is usually formed in the manner just described, and the generic name of those containing less oxygen is similar but ends in *-ite* instead of in *-ate*. If the same element forms more than two classess of salts, the prefixes *hypo-* and *per-* are employed as further means of distinction, or occasionally some special system of nomenclature is adopted. The following examples will illustrate the application of these rules to particular cases:

$KNO^2$ = Potassic nitrite or Nitrite of potassium.
$AgNO^2$ = Argentic nitrite or Nitrite of silver.
$KNO^3$ = Potassic nitrate or Nitrate of potassium.
$AgNO^3$ = Argentic nitrate or Nitrate of silver.
$Ba(NO^3)^2$ = Barytic nitrate or Nitrate of barium.
$KClO$ = Potassic hypochlorite or Hypochlorite of potassium.
$KClO^2$ = Potassic chlorite or Chlorite of potassium.
$KClO^3$ = Potassic chlorate or Chlorate of potassium.
$KClO^4$ = Potassic perchlorate or Perchlorate of potassium.
$K^2S^2O^3$ = Potassic hyposulphite or Hyposulphite of potassium.
$K^2SO^3$ = Potassic sulphite or Sulphite of potassium.

$K^2S^2O^6$ = **Potassic hyposulphate or Hyposulphate of potassium.**
$K^2SO^4$ = **Potassic sulphate or Sulphate of potassium.**

In a few cases, names formed in the same manner as these are given to salts which differ otherwise than in the mere proportion of oxygen that they contain: for instance—

$KH^2PO^2$ = **Potassic hypophosphite or Hypophosphite of potassium.**
$K^2HPO^3$ = **Potassic phosphite or Phosphite of potassium.**
$K^3PO^4$ = **Potassic phosphate or Phosphate of potassium.**

These three classes of salts differ, as will be observed, in respect to the quantity of hydrogen as well as of oxygen which they contain. The explanation of the anomaly presented by their nomenclature is to be sought for in the history of the views that have been held at various times regarding their constitution.

The nomenclature of mixed salts, that is, of salts containing more than one metal or more than one radicle, is a little more complicated than that of such as precede, but it will be easily understood from a few examples: *e. g.*—

$KHSO^4$ = **Hydro-potassic sulphate or Sulphate of hydrogen and potassium.**
$KAl(SO^4)^2$ = **Alumino-potassic sulphate, or Sulphate of aluminium and potassium.** (In the name of this salt it is not needful to specify that it contains *twice* the group $SO^4$, this being already implied when it is stated that each molecule contains an atom of potassium and an atom of aluminium, the sum of whose atomicities is *four* = twice the atomicity of the group $SO^4$. A similar remark applies in a great many other cases.)
$Al^2(SO^4)O^2$ = **Aluminic sulphato-dioxide.***
$Fe^2(SO^4)^2O$ = **Ferric disulphato-oxide.***
$PbH(NO^3)O$ = **Hydro-plumbic nitrato-oxide,*** or **Plumbic hydrato-nitrate.**
$BiH^2(NO^3)O^2$ = **Dihydro-bismuthic nitrato-dioxide.***
$Ba(C^2H^3O^2)(NO^3)$ = **Barytic acetato-nitrate or nitrato-acetate.**
$Pb(C^2H^3O^2)Cl$ = **Plumbic acetato-chloride.***

The systematic names of the hydrogen-salts are of course similar to those of the corresponding salts of other metals; these names, however, are not very commonly used: it is more usual to speak of the hydrogen-salts as *acids*. Thus, for example, $HNO^3$ is more frequently called **nitric acid** than **hydric nitrate**, $H^2SO^4$ more frequently **sulphuric acid** than **hydric sulphate**, &c. With regard to the nomenclature of the acids, the following rules are observed: if the systematic name of a hydrogen-salt is *hydric —ate*, its common name is *—ic acid*; and if its systematic name is *hydric —ite*, its common name is *—ous acid*: examples—

| Systematic names. | Common names. |
|---|---|
| Hydric hypochlorite. | Hypochlorous acid. |
| Hydric chlorite. | Chlorous acid. |
| Hydric chlorate. | Chloric acid. |
| Hydric perchlorate. | Perchloric acid. |

Similarly, mixed salts of hydrogen and any other metal are frequently called *acid salts*: *e. g.*, **hydro-potassic sulphate**, $KHSO^4$, is often called **acid sulphate of potassium**; and **dihydro-potassic phosphate**, $KH^2PO^4$, is often called **diacid phosphate of potassium**. On the other hand, mixed salts formed by the union of the type oxide with the type of any simple salt, whether containing hydrogen or not, are often called *basic salts*, *e. g.*, **plumbic dioxi-dinitrate**, $Pb^3(NO^3)^2O^2$, and plumbic hydrato-nitrate are each of them called **basic nitrate of lead**; in like manner, ferric oxi-disulphate, $Fe^2O(SO^4)^2$, and **ferric dioxi-sulphate**, $Fe^2O^2(SO^4)$ are called **basic ferric sulphates**, or basic sulphates of iron. Such names as these are often convenient when speaking of certain well-known compounds, but for scientific purposes they are better avoided.

When a metal forms two series of oxygen-salts of the same generic name, the salts of the two series are distinguished in the same manner as the various oxides, chlorides, &c., of the metal. Thus we speak of **mercurous nitrate** and **mercurous sulphate**, **mercuric nitrate** and **mercuric sulphate**; **ferrous sulphate** or protosulphate of iron and ferric sulphate or sesquisulphate of iron; &c. &c.

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* Strictly speaking, the names of these salts would be equally correct if inverted thus: *aluminic dioxi-sulphate*, *ferric oxi-disulphate*, *hydro-plumbic oxi-nitrate*, *plumbic chloro-acetate*, &c.; but inconvenience might arise from the use of names such as these, inasmuch as the corresponding terms in the case of certain organic salts would very closely resemble the names of totally distinct compounds: for instance, an *oxi-benzoate* or *dioxi-benzoate* would be very apt to be confounded with an *oxybenzoate* or *dioxybenzoate*, a *chloro-acetate* with a *chloracetate*, &c. &c.

Oxygen-salts being in reality merely a particular class of oxides, there are of course corresponding chlorides, nitrides, &c., of the same radicles. The nomenclature of these compounds has never hitherto assumed a very fixed or systematic form, radicles supposed to be contained in the various classes of salts having been named, one by one, according to no general system, by the investigators of the compounds of each. Thus the radicle PO supposed to be contained in the phosphates is called *phosphoryl;* but the radicles of the phosphites and hypophosphites have no recognised names; the radicle $SO^2$ of the sulphates is called *sulphuryl;* and the radicle SO of the sulphites is called *thionyl;* again, the radicle $NO^2$ of the nitrates is called *nitryl*, and the radicle NO (monatomic) of the nitrites is called *nitrosyl* or *azotyl*. From these examples it will be seen that there is no certain rule by which the name of a class of salts being given, that of the radicle, supposed upon the theory of types to be contained in them, can be deduced. In these circumstances we may venture to suggest the following rule as applicable to such cases: to form the name of the radicle of any class of salts, *substitute the termination* -yl *for the final* e *in the generic name of the salts in question.* According to this rule we should have such names as the following:

| Names of Salts. | Names of Radicles required by typical formulæ. |
|---|---|
| Phosphates. | Phosphatyl. |
| Phosphites. | Phosphityl. |
| Sulphates. | Sulphatyl. |
| Sulphites. | Sulphityl. |
| Nitrates. | Nitratyl. |
| Nitrites. | Nitrityl. |

When the termination *-ic* is added to the name of a radicle in order to form the name of a compound containing it, the syllable *yl* may generally be elided: thus—

$POCl^3$ = Phosphatic chloride or Chloride of phosphatyl.

$SO^2Cl^2$ = Sulphatic chloride or Chloride of sulphatyl.

$SOCl^2$ = Sulphitic chloride or Chloride of sulphityl.

$\left.\begin{matrix}SO^2Cl\\HO\end{matrix}\right\}$ = Hydro-sulphatic oxichloride or Sulphatic chloro-hydrate.

The nomenclature of the compounds formed when oxygenated radicles replace hydrogen in the type $H^3N$ or its multiples, or in the mixed type $\left.\begin{matrix}aH^2O\\bH^3N\end{matrix}\right\}$, in regard to which special rules are followed to some extent, will be found fully set forth in the articles AMIC ACIDS (i. 165) and AMIDES (i. 169).

Compounds containing two or more atoms of the same polyatomic radicle in one molecule, and resulting from the combination of two or more molecules of the simpler compounds of the radicles, as explained in the article CLASSIFICATION (i. 1020—1022), may be distinguished by prefixing to the names of the simplest corresponding compounds the syllables *di-*, *tri-*, &c.: for example—

$K^2S^2O^7$ = Potassic disulphate.

$K^2Cr^2O^7$ = Potassic dichromate.

$Na^4P^2O^7$ = Tetrasodic diphosphate (Pyrophosphate of sodium).

$Na^2P^2O^6$ = Disodic diphosphate (Insoluble metaphosphate).

$Na^3P^3O^9$ = Trisodic triphosphate (Fleitmann and Henneberg's metaphosphate.)

The so-called *sulphur-salts* which represent oxygen-salts wherein the oxygen is replaced to a greater or less extent by sulphur, may be named in precisely the same way as the corresponding oxygen-salts by prefixing sulpho- to the names of the latter, and also, when needful, a numerical prefix to indicate the extent to which the replacement has proceeded.

### NOMENCLATURE OF ORGANIC BODIES.

In organic chemistry we have to do with many hundreds of substances formed of the same three or four elements. It would therefore be an utterly hopeless task to try to frame for each substance a name like those of inorganic compounds, which, if they do not directly express the composition of the bodies to which they are applied, have at least a definite relation thereto. A classification of organic bodies with reference to their composition alone, would be far from affording an adequate expression of their nature and mutual relations: hence a systematic nomenclature for them can be founded only on a classification which takes cognisance of other characters in addition to mere composition. Such a classification must be founded, first of all, upon the fact that almost all well-investigated organic compounds are found to admit of being arranged in groups, which, although they may differ greatly in many important respects, exhibit a certain correspondence in the relations which their several members bear to each other. These groups again admit of division and subdivision into smaller and smaller groups, the individual members of which are more and more closely related to each other, until we come to substances which are as intimately connected together by composition and properties as the different salts containing the same metal or the same oxygen-radicle.

Thus, the great majority of organic compounds (we are of course speaking only of those which have been sufficiently investigated to allow of a definite position being assigned to them) belong to one or other of the two great series—the Fatty Series, and the Aromatic Series. Each of these series again consists of a number of groups, each of which reflects more or less completely the character of all the rest. And each group in its turn consists of a number of alcohols and acids, around which, as central compounds, we have to classify hydrocarbons, ethers, salts, amides, alkaloïds, and numerous other derivatives.

Taking the alcohols as representing also the corresponding ethers and amines and their other immediate derivatives, and the hydrogen-salts or acids to stand for all other salts of the same name with their derivatives, the leading terms of the several groups belonging to each homologous series may be arranged as in the following table; where, for the sake of clearness, the formulæ of compounds belonging to a particular group, the tritylic, are given (instead of general formulæ applicable to any group whatever), but in order to fill up the scheme, such terms as are not known in this group are represented by examples borrowed from other analogous groups.[*]

| | Alcohols. | Acids. | | | |
|---|---|---|---|---|---|
| | | *Monobasic.* | | | |
| Mon-atomic. | $C^3H^8O$<br>Tritylic alcohol. | $C^3H^6O^2$<br>Propionic acid. | $C^3H^4O^3$<br>Pyruvic acid. | $C^3H^2O^4$<br>($C^4H^2O^4$ = mellitic acid). |
| | | | *Dibasic.* | |
| Di-atomic. | $C^3H^8O^2$<br>Tritylic glycol. | $C^3H^6O^3$<br>Lactic acid. | $C^3H^4O^4$<br>Malonic acid. | $C^3H^2O^5$<br>Mesoxalic acid. |
| Tri-atomic. | $C^3H^8O^3$<br>Glycerin. | $C^3H^6O^4$<br>Glyceric acid. | $C^3H^4O^5$<br>Tartronic acid. | *Tribasic.*<br>$C^3H^2O^6$<br>($C^6H^6O^6$ = aconitic acid). |
| Tetr-atomic. | $C^3H^8O^4$<br>($C^4H^{10}O^4$ = erythromannite). | $C^3H^6O^5$<br>($C^7H^6O^5$ = gallic acid). | $C^3H^4O^6$<br>($C^4H^6O^6$ = tartaric acid). | $C^3H^2O^7$<br>($C^6H^8O^7$ = citric acid). |

A table similar to the above has already been given in the article ACIDS (i. 53), in which place further details will also be found respecting the compounds represented by the special examples here given.

The homologous series to which each such group belongs is determined by the ratio of carbon to hydrogen in its individual terms, and its position in that series by the number of atoms of carbon which they contain; while the position in the group of the several terms themselves is determined by their entire composition and general chemical functions.

Any particular compound is accordingly completely characterised when we know to what group it belongs and what is its place in that group. This then is the information which it is required that the names of a really systematic and rational nomenclature should give us, concerning the substances to which they are applied: and it would seem by no means impossible to form names which should completely satisfy these requirements, by making the *root* of each name denote the group, and the *termination* or a second word denote the function. Such a nomenclature would correspond precisely with the typical system of rational formulæ; for, as has been shown in other articles (CLASSIFICATION, i. 1022; FORMULÆ, ii. 700), these formulæ express by means of radicles the group or genetic relations of the substances they represent, and by means of types their chemical functions. Or, again, such a nomenclature would correspond with the binomial nomenclature of the natural-history sciences, according to which each animal or plant is distinguished by means of two Latin words, one indicating its *genus*, the other its *species*. An attempt at a systematic nomenclature for organic compounds based on these principles is contained in the paper referred to in the last foot-note; which, though not sufficiently successful to make it worth while to reproduce it here, we allude to, because we are convinced that it is in this direction, if at all, that a rational nomenclature is to be reached.

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[*] So far as the writer is aware, this mode of classifying organic substances was first published in a paper on the Nomenclature of Organic Compounds which he read before the Chemical Section of the British Association, at its meeting in Dublin, September 1857 (see Brit. Assoc. Rep., 1857, Notices and Abstracts, p. 45); but before the appearance of the paper referred to in the printed form, a similar system of classification was suggested by Kekulé (Ann. Ch. Pharm. cvi. 158. May, 1858).

The existing nomenclature of organic chemistry fulfils to a considerable extent, in a more or less satisfactory manner, the requirements of a rational nomenclature as these are indicated above; it however still retains a good many habits of naming, as well as individual names, inherited from the early days of the science, when it was impossible to foresee either the direction or the extent of its subsequent development, and hence possesses many terms formed without much reference to anything but the fancy of individual chemists and their taste in the choice of euphonious words. But the greatest defects of this nomenclature arise from the want of unanimity among chemical discoverers and systematisers as to the manner in which the principles, recognised more or less distinctly by all, should be carried out. And this want of unanimity, we cannot help thinking, is mainly due, not to the intrinsic difficulty of the subject, so much as to the too partial manner in which it is generally considered—reforms being often attempted in particular departments, without sufficient thought being given to the effect which they would have if consistently extended to the nomenclature of other parts of the science.

In describing the nomenclature of organic chemistry, as it at present exists, we shall consider first the methods employed to designate the several *groups*, and then the modes of indicating the various chemical *functions*.

*Nomenclature of Groups.*—By reference to the example of a chemical group already given on page 128, it will be seen that the names of its leading terms exhibit very little relation to one another: we have tritylic alcohol and tritylic glycol, glycerin and glyceric acid, malonic acid and tartronic acid, but all the other names might have been selected completely at random. And on examining the nomenclature of any other group, the state of things would be found very much the same. The fact is, that throughout every department of organic chemistry the general course of discovery has been such that substances became known and required to be named one by one, long before the relations of each to the rest could be ascertained. Hence, very closely related substances often bear names which exhibit no trace whatever of their connexion: as alcohol, ether, and acetic acid; propionic acid, lactic acid, and glycerin; succinic acid, malic acid, and tartaric acid. Such names as these it would be very difficult to get rid of, and when they are (as in these examples) convenient in themselves and universally adopted, there is no reason for wishing to do so. In fact, it often happens that such names are practically better than those which at first sight appear more systematic. For instance, nothing could seem more natural than to call the acid $C^3H^6O^4$ resulting from the oxidation of glycerin, $C^3H^8O^3$, *glyceric acid*, a name which at once recalls its connexion with the substance from which it is derived. But according to the established usage of organic chemistry, the radicle of this acid, $C^3H^3O$, corresponding to its typical formula $\left.\begin{matrix}C^3H^3O\\H^3\end{matrix}\right\}O^3$, would be called *glyceryl*, a name which already belongs to $C^3H^5$, the radicle of glycerin. We might thus have the two compounds $C^3H^5Cl^3$ and $C^3H^3OCl^3$ both of them denoted by the name, chloride of glyceryl, or glycerylic chloride, a confusion which could not have arisen had there been less similarity in the names of the primary compounds. Indeed it is by no means desirable to introduce much more regularity than at present exists into the nomenclature of the principal members of each group, unless some effectual system of differentiating each member and its derivatives, equivalent to what was attempted in the paper already referred to, is adopted at the same time.

Of late years methods of naming, possessing a certain degree of generality, have come into partial use, for some corresponding terms of different groups. Thus, the monatomic alcohols and one or two of their most immediate derivatives, in most of the groups of the first homologous series, have names whose root is formed by a Greek numeral: as tritylic, tetrylic, hexylic, heptylic, &c. alcohols; tritylene, tetrylene, hexylene, heptylene, &c. Another expedient which has been a good deal employed to indicate the existence of a genetic connexion between different bodies, but without defining its nature, consists in making the name of one body out of an anagram of that of another: as meconic and comenic, aconitic and itaconic, narcotine and cotarnine, lep(idine) and pel(amine), pelarg(onic) and leparg(ylic), salylic and lasylic, &c.

The system so much followed in the nomenclature of other sciences, of giving names in honour of discoverers or other eminent men, has not been much employed in chemistry, and we do not think that this forms any ground for regret. Among organic compounds, *dumasin* is almost the only one which bears a name of this kind: *maclurin*, which has the appearance of being another name of the same class, is one for which no chemist is responsible so much as the botanist who called fustic *Maclura tinctoria*. Such names again as *herapathite* and *weltzienite* have generally originated, not with chemists, but with crystallographers, who have given them in accordance with their mineralogical habitudes.

One rule which chemists would do well to attend to in their choice of names, is to avoid such as suggest a connexion that does not exist: such as metamorphine, pseudomorphine, hypogæic acid, the last of which (from *Arachis hypogæa*) seems to imply the existence of a more highly oxygenated "gæic" acid.

*Nomenclature of Functions.*—The chemical functions of organic substances are generally denoted either by using in a generalised sense the proper names of the substances in which the several functions were first distinctly recognised, as methylic alcohol, butyric aldehyde, valeric acetone, amylic glycol, &c.; or by systematic names formed on the analogy of the nomenclature of mineral chemistry, as methylic hydrate or hydrate of methyl, methylic chloride or chloride of methyl, methylic acetate or acetate of methyl, &c.; or lastly, by means of terminations, as methol for methylic alcohol, butyral for butyric aldehyde, valerone for valeric acetone, oxalurethane for oxalic urethane, lactamethane for lactic urethane or carbamethane, ethylene, amylene, &c.: this last method may for the most part be regarded as a contracted form of the first.

We will briefly discuss the names in actual use for compounds representing the leading terms of a chemical group as above defined, and for their principal derivatives, endeavouring to point out those which it is most advisable to employ.

ALCOHOLS. 1. *Monatomic.*—These are either named alcohols or hydrates, with another word added to distinguish the group to which they belong, this word in almost all cases ending in *-ylic*, as methylic alcohol, methylic hydrate, or hydrate of methyl; benzylic alcohol, benzylic hydrate, or hydrate of benzyl. The termination *-ol*, to indicate the alcoholic function, is more employed by French than by English chemists. The nomenclature of derivatives of the alcohols will be most clearly and concisely explained by special examples, thus:

| *Function.* | *Formula.* | | *Names.* |
|---|---|---|---|
| Alcohol . . | $C^2H^6O$ | = | Ethylic hydrate, &c. (as above). |
| Radicle . . | $C^2H^5$ | (= | alcohol − HO) = Ethyl. |
| Hydrocarbon . | $C^2H^4$ | (= | alcohol − $H^2O$) = Ethylene. |
| Ether . . | $C^4H^{10}O$ | = | Ethylic ether, or ethylic oxide. |
| Compound ethers | $C^2H^5Cl$ | = | Ethylic chloride, or chloride of ethyl. |
| | $C^2H^5(C^2H^3O^2)$ | = | Ethylic acetate, or acetate of ethyl. |
| | $(C^2H^5)HSO^4$ | = | Hydro-ethylic sulphate, or sulphate of ethyl and hydrogen; also called ethyl-sulphuric acid, or sulphethylic acid. |
| | $(C^2H^5)^2SO^4$ | = | Ethylic sulphate, or sulphate of ethyl. |
| Alkaloïds . . | $(C^2H^5)H^2N$ | = | Ethylamine, or dihydro-ethylic nitride. |
| | $(C^2H^5)^2HN$ | = | Diethylamine, or hydro-diethylic nitride. |
| | $(C^2H^5)^3N$ | = | Triethylamine, or triethylic nitride. |
| | $(C^2H^5)^3P$ | = | Triethylphosphine, or triethylic phosphide. |
| Metallic derivatives. | $C^2H^5ZnI$ | = | Zinc ethylo-iodide, or ethylo-iodide of zinc. |
| | $(C^2H^5)^2Zn$ | = | Zinc ethylide, ethylide of zinc, or zinc-ethyl. |
| | $(C^2H^5)^2Hg$ | = | Mercuric ethylide, ethylide of mercury, or mercury-ethyl. |

(Such names as hydrochloric ether, acetic ether, &c., are not given above, because though used for the ethers of this group, they have no analogues in other cases.)

Of the various names above given for single compounds, we believe that those which stand first in order—that is, names of the form *ethylic hydrate, ethylic oxide, ethylic acetate*, &c., in general deserve the preference. Names formed by the generalisation of special names are convenient enough sometimes, but this method of nomenclature is not well adapted for application in all cases, the names which it leads to being often clumsy in themselves and giving rise to still clumsier derivatives and compound names. On the other hand, such names as ***hydrate of ethyl, oxide of ethyl, chloride of ethyl***, &c., seem to belong too exclusively to one view of the constitution of the bodies they denote; whereas names such as those to which we have given the preference (ethylic hydrate, &c.), while quite in accordance with this view, may still be used independently of it. They would remain equally applicable and would be equally intelligible, though chemists should cease to recognise the existence of ethyl or similar radicles as proximate constituents of the alcohols, for they do not of necessity imply anything more than that the compounds $C^2H^6O$, $C^4H^{10}O$, $C^2H^5Cl$, &c., belong to the ethylic group, and that they bear to each other the same mutual relations that the compounds $KHO$, $K^2O$, $KCl$, &c., do in the potassic group.

In the nomenclature of the so-called acid ethers, such as $(C^2H^5)HSO^4$, &c., it would be well to let the name of the alcoholic constituent always precede that of the acid,—that is, to say ethyl-sulphuric acid, ethyl-sulphate, &c., and not sulphethylic acid, sulphethylate, &c. For not only is the saline character of such compounds not due to the alcohol portion of their constituents, as seems to be implied if this is named last and so receives the saline termination, but confusion may actually arise from the use of *sulpho-* as a prefix in this sense and also to denote replacement of oxygen by sulphur (in such names as ***sulphocarbonate***, for instance).

Compounds belonging to more than one alcoholic group are easily named in accordance with the examples given above, by following the analogy of the nomenclature of the mixed compounds of mineral chemistry. For instance:

$(CH^3)(C^2H^5)O$ = Methyl-ethylic oxide.
$(C^2H^5)(C^5H^{11})SO^4$ = Ethyl-amylic sulphate.
$(CH^3)(C^2H^5)(C^5H^{11})N$ = Methyl-ethyl-amylamine.
Similarly $K(C^2H^5)O$ is Potassio-ethylic oxide.

But just as the name potassio-hydric oxide may be abbreviated into potassic hydrate, so the names of many corresponding organic compounds may be abbreviated: as methyl-ethylic oxide into methylic ethylate, potassio-ethylic oxide into potassic ethylate, &c.

2. *Diatomic alcohols.*—The first discovered of these compounds, $C^2H^6O^2$, was called "glycol," from the first syllable of *glycerin* and the last of *alcohol*, to recall the fact of its being chemically intermediate between these two bodies, and this name has since been employed as a general term for all compounds of this class. A more systematic name than glycol would have been ethylenic hydrate, or hydrate of ethylene, and names of this form are the most suitable for general application: as tritylenic hydrate, or hydrate of tritylene, amylenic hydrate or hydrate of amylene.

Those derivatives of the diatomic alcohols which correspond to derivatives of the monatomic alcohols, are named in the same way as the latter, the only difference being that the adjectival portion of the name ends in *-ylenic* instead of in -ylic, or when the adjective is replaced by a substantive preceded by *of*, this substantive ends in *-ylene* instead of in -yl: as

$C^2H^4O$ = Ethylenic oxide, or oxide of ethylene.
$C^2H^4Cl^2$ = Ethylenic chloride, or chloride of ethylene.
$C^2H^4(C^2H^3O^2)^2$ = Ethylenic acetate, or acetate of ethylene.
$(C^2H^4)H^4N^2$ = Ethylenediamine.
$(C^2H^4)^2H^2N^2$ = Diethylenediamine.

Derivatives which have no precise analogues among those of the monatomic alcohols are easily named upon the analogy of corresponding mineral compounds: as—

$(C^2H^4)^2O^2$ = Diethylenic dioxide.
$(C^2H^4)^2H^2O^3$ = Dihydro-diethylenic oxide (also called *diethylenic alcohol*).

$$\left.\begin{array}{r}C^2H^4Cl\\HO\end{array}\right\} = \text{Ethylenic hydrato-chloride (monochlorhydrin of glycol).}$$

$$\left.\begin{array}{r}C^2H^4\\(C^2H^3O)H\end{array}\right\}O^2 = \text{Ethylenic hydrato-acetate (monacetin of glycol).}$$

$$\left.\begin{array}{r}C^2H^4Cl\\(C^2H^3O)O\end{array}\right\} = \text{Ethylenic acetato-chloride (acetochlorhydrin of glycol).}$$

The names enclosed in parentheses (monochlorhydrin of glycol, &c.) are borrowed from the nomenclature of the derivatives of glycerin; this system applied to other diatomic alcohols, gives rise to names even more cumbrous than these: as, monochlorhydrin of tritylic glycol.

3. *Triatomic alcohols.*—The only triatomic alcohol known with any certainty is

glycerin, the nomenclature of whose derivatives follows for the most part special rules. The compound ethers of glycerin are denoted by names formed from those of the acids by means of the termination *-in* and a numerical prefix when needful: as—

Monostearin.
Distearin.
Tristearin.
Tributyrin.

Chlorhydrin.
Dichlorhydrin.
Benzochlorhydrin.
Aceto-dichlorhydrin.

Glycerin yields also another set of derivatives, bearing the same relation to these normal compounds that the monobasic metaphosphates do to the ordinary phosphates: that is to say, each of them differs by the elements of a molecule of water from a normal glycerin-compound. The nomenclature of these is as follows—

$C^3H^6O^2 = C^3H^8O^3 - H^2O$ = Glycide.
$C^3H^5OCl = C^3H^7O^2Cl - H^2O$ = Chlorhydroglycide (epichlorhydrin).
$C^3H^5(C^2H^5)O^2 = C^3H^7(C^2H^5)O^3 - H^2O$ = Ethylglycide.

It will be seen that the nomenclature of glycerin and its derivatives is not such as to admit of very ready extension to other similar compounds; names for these might, however, be easily formed by following the analogy of the nomenclature for inorganic salts already explained.

The derivatives of other polyatomic alcohols that have been hitherto studied, belong almost exclusively to the class of compound ethers. They are named by combining with the name of the alcohol that of the generating acid: as stearo-glucose, butyro-glucose; diaceto-mannitan, tetrabutyro-mannitan, chlorhydro-mannitan.

For further illustrations of the nomenclature of the alcohols and their derivatives, see the articles ALCOHOLS (i. 97) and ETHERS (ii. 508).

ACIDS.—The nomenclature of all such derivatives of the organic acids as have analogues among the derivatives of mineral acids, is precisely similar to the nomenclature of the latter; we may therefore consider it as having been already sufficiently discussed.

It may however be pointed out that, inasmuch as the name of each class of organic salts is in general independent of that of every other class, the corresponding oxygenated radicles can be denoted by shorter names than those which, as we have pointed out, are often necessary for the inorganic radicles. Thus to get the name of the radicle of an organic salt, we change the termination *-ate* (*-ite* does not occur unless quite exceptionally, as salicylite of methyl) into *-yl*, instead of retaining the *-at* of the name of the salt: for instance benzoyl, instead of benzoatyl, acetyl,* instead of acetatyl, &c.

It is still needful to say a few words upon the nomenclature of the so-called substitution-derivatives and conjugated derivatives of the organic acids, and what is here said may be taken as also for the most part applicable to the corresponding derivatives of the alcohols.

Compounds formed by the substitution of chlorine, bromine, &c., for hydrogen are denoted by prefixing *chloro-*, *dichloro-*, *bromo-*, *dibromo-*, &c., to the names of the corresponding normal compounds; and bodies in which the groups $NO^2$, $NH^2$, &c., replace hydrogen are similarly named by means of the prefixes *nitro-*, *amido-*, &c.: as,

Chloracetic acid.
Dibromosuccinic acid.

Nitrobenzoic acid.
Diamidobenzoic acid.

The prefix *oxy-* is commonly used in a somewhat different sense, namely to express the addition of oxygen, not the replacement of hydrogen thereby: as

$C^7H^6O^2$ = Benzoic acid.
$C^7H^6O^3$ = Oxybenzoic acid.

$C^7H^6O^3$ = Salicylic acid.
$C^7H^6O^4$ = Oxysalicylic acid.
$C^7H^6O^5$ = Dioxysalicylic acid.

The application of this prefix may however be considered as comparable to that of the others above mentioned, if, with Kolbe, we regard the addition of oxygen in these cases to be effected by the replacement of H by HO.

Sometimes, instead of the prefix *amido-*, the termination *-amic* is employed, as benzamic acid, instead of amidobenzoic acid; such names are, however, incorrect: for monobasic acids such as benzoic, do not form true amic acids, and the compounds referred to do not, even in respect to empirical composition, bear the same relation to the normal compounds that oxamic acid, for instance, does to oxalic acid. Strictly speaking, the so-called amido- acids, or amic acids of monobasic organic acids, are most closely related to the oxygenated derivatives of the bodies with which they are commonly compared, so that the true systematic name of amidobenzoic or benzamic acid would be *oxybenzamic acid* (see also Amic Acids, i. 167).

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* The name *acetyl* was first given to the group $C^2H^3O$ by Dumas (*Traité de Chim. appl. aux arts*, vol. vi. p. 341, 1843), who represented aldehyde by the formula $C^2H^3O.H$, calling it "hydrure d'acétyle." Williamson, who first suggested the views now prevalent respecting the constitution of acetic and other similar acids, called this radicle "othyl;" but this name has been generally abandoned for the term acetyl (again applied by Gerhardt as it had been by Dumas), on account of the difficulty of forming analogous names for analogous radicles.

The prefix *sulpho-* is also often applied to the names of organic acids in a manner which is not quite correct: thus, the substance called sulphacetic acid is not, what the name would best express, a body derived from acetic acid by the substitution of sulphur for oxygen, but a compound produced by the action of sulphuric anhydride on acetic acid. This product would be better named acetosulphuric acid than sulphacetic acid, but even that name would not be quite correct, inasmuch as the substance in question is primarily related to glycollic (oxyacetic) acid and not to acetic acid.

Several derivatives of the types $nH^3N$ and $\left.\begin{matrix}H^3N\\H^2O\end{matrix}\right\}$ containing the radicles CO, carbonyl, and $C^2H^2O$, glycollyl, have received special names in addition to their systematic names: for instance, carbamide, $\left.\begin{matrix}CO\\H^4\end{matrix}\right\}N^2$, is also called *urea*, and this name is often applied in a generic sense to all compounds derived from urea by partial or complete replacement of its hydrogen by other radicles, as $\left.\begin{matrix}CO\\(C^2H^5)H^3\end{matrix}\right\}N^2$ *ethyl-urea*, $\left.\begin{matrix}CO\\(C^2H^3O)^2H^2\end{matrix}\right\}N^2$ = diacetyl-urea. Similarly, acids formed upon the type of hippuric acid, that is, by the replacement of hydrogen in glycollamic acid (glycocine), $\left.\begin{matrix}C^2H^2O\\H^3\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, are often denoted by names ending in *-uric*, as salicyluric acid, cuminuric acid, toluyluric acid. Exceptional names are also used to some extent for the compound ethers corresponding to amic acids: thus ethylic carbamate is also called *urethane* or *carbamethane*, ethylic oxamate is also called *oxamethane*, ethylic lactamate is also called *lactamethane*, &c.

We give below a list of other terminations to which particular significations are often attached, together with examples illustrating the use of each.

**-al.** Abbreviation of aldehyde. Ex. *Butyral* = butyric aldehyde; *valeral* = valeric aldehyde.

**-anil.** (fr. aniline). Phenyl- —imide. Ex. *Malanil* = phenyl-malimide.

**-anilic acid.** Phenyl- —amic acid. Ex. *Succinanilic acid* = phenyl-succinamic acid.

**-anilide.** Phenyl- —amide. Ex. *Acetanilide* = phenyl-acetamide.

**-ene.** A compound containing only carbon and hydrogen. Ex. *Benzene, naphthalene.*

**-ide.** (1) A compound of two elements, two radicles, or of an element and a radicle. Ex. *Zinc-methide*, or *zinc-methylide*; *methylic ethide.* (2) A termination proposed by **Gerhardt** (*Système unitaire*,) as a general mode of denoting anhydrides: it is still in partial use in this sense. Ex. *Glycollide, lactide, mannide.* (3) A general term for compound ethers of polyatomic alcohols. Ex. *Glycerides, glucosides, mannitanides.* Seldom used to denote individual substances.

**-in.** (1) A neutral compound of carbon, hydrogen, and oxygen. Ex. *Glycerin, salicin, meconin.* (2) A compound ether of glycerin. Ex. *Chlorhydrin, palmitin.*

**-ine.** An alkaloïd. Ex. *Morphine, quinine.* Also used by some writers, but not in this work, in the same sense as *-ene*, or *-in*; as benzine for benzene, glycerine for glycerin.

**-itan.** Employed by Berthelot to denote the first product obtained by dehydrating a sugar whose name ends in *-ite.* Ex. *Mannitan, dulcitan.*

**-ite.** A saccharine compound containing more hydrogen than would be required to convert all the oxygen into water. Ex. *Mannite, dulcite, pinite.*

**-ol.** Abbreviation of alcohol. Ex. *Phenol* = phenylic alcohol; *menthol* = menthylic alcohol.

**-ole.** Sometimes used instead of *-ene*, to denote hydrocarbons. Ex. *Benzole* for benzene, *toluole* for toluene. Not used in this work.

**-one.** (1) Abbreviation of acetone or ketone. Ex. *Valerone* = valeric ketone; *benzone* = benzoic ketone. (2) A termination much employed without definite meaning. Ex. *Quinone, indifuscone.*

**-ose.** A saccharine compound containing oxygen and hydrogen in the proportion required to convert each completely into water. Ex. *Glucose, saccharose, lactose.*

**-yl.** A compound radicle. Ex. *Ethyl, benzoyl, benzyl.*

**-ylene.** A hydrocarbon (diatomic radicle) containing 1 at. hydrogen less than the radicle of corresponding name ending in -yl. Ex. *Ethylene, tritylene, benzylene.* (This termination is sometimes used in a manner which is not in strict accordance with the above rule: thus the hydrocarbons of the series $C^nH^{2n-2}$ are called *acetylene, allylene, crotonylene, valerylene*, among which names allylene is the only one that agrees with the general rule. Some general system of naming the hydrocarbons homologous with marsh-gas is a great desideratum.)

For further information respecting the history of chemical nomenclature and various attempts that have been made from time to time to render it more systematic, see, in addition to the references already given, the following: Kopp, Geschichte der Chemie, ii. 412 *et seq.* Berzelius, Lehrbuch der Chemie, edit. 1831, vol. iv. (2nd part) pp. 956, 957; also (for a much fuller treatment of the subject) edit. 1841, vol. x. pp. 428–449. Dumas, Leçons sur la Philosophie Chimique, pp. 321–358. Boset, Berzelius's Jahresber. xxiii. 23, 24. Gmelin, Handbook of Chemistry, vii. 149–153. Griffin, Chemical Recreations, 7th ed. (1834), pp. 234–274; also (another system) Radicle Theory in Chemistry (1858), pp. 86–90. Newlands, Chemical News, iv. 281 (30th Nov. 1861). Williamson, Chem. Soc. J. xvii. (new series, ii.) 421. The foregoing relate to chemical nomenclature in general; the following more particularly to the nomenclature of organic compounds: Laurent, Chemical Method, pp. 356 *et seq.* Daubeny, Rep. Brit. Associat. 1851; Transactions of Sections, p. 124. Weltzien, Systematische Zusammenstellung der organisch. Verbindungen (1860), pp. xxv.–xxviii. Berthelot, Chimie organique fondée sur la synthèse (1860), i. 180–186. Kolbe, Lehrbuch d. organisch. Chemie, i. 53–62.

G. C. F.

**NONTRONITE.** A hydrated ferric silicate allied to chloropal, which it closely resembles in physical and chemical properties, excepting that it gelatinises with acids. Its composition is shown by the following analyses:

*a.* From Nontron, Dep. Dordogne, France (Berthier, Ann. Ch. Phys. [2] xxxv. 92).—*b.* Villefranche (Dufrénoy, Ann. Min. [3] iii. 393).—*c.* Montmors, near Autun (Jacquelain, Ann. Ch. Phys. [2] xli. 101).—*d.* Andreasberg in the Hartz (Biewend, J. pr. Chem. xi. 162).—*e.* Tirschenreuth (H. Müller, *Dana's Mineralogy*, ii. 337).—*f.* From the same locality (Uricoechea, *loc. cit.*):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|
| Silica . . | 44·0 | 40·68 | 41·31 | 41·10 | 47·10 | 47·59 |
| Alumina . . | 3·6 | 3·96 | 3·31 | . . | 7·15 | 42·49 |
| Ferric oxide . | 29·0 | 30·19 | 35·69 | 37·30 | 35·75 | |
| Magnesia . . | 2·1 | 2·37 | $Cu^2O$ 0·90 | . . | . . | $Mg^2O$ 0·13 |
| Lime . . . | . . | . . | 0·19 | | | |
| Water . . . | 18·7 | 23·00 | 18·63 | 21·56 | 10·00 | 9·79 |
| Clay . . . | 0·1 | | | | | |
| | 97·5 | 100·20 | 100·03 | 99·96 | 100·00 | 100·00 |

**NONYL.** $C^9H^{19}$.—The ninth term of the series of alcohol-radicles, $C^nH^{2n+1}$. It is also called *Pelargonyl*, but that name belongs more properly to the corresponding acid-radicle, $C^9H^{17}O$, homologous with acetyl, $C^2H^3O$.

Nonyl has not yet been isolated. *Hydride of nonyl*, $C^9H^{20}$, occurs, together with nonylene, $C^9H^{18}$, and many other hydrocarbons of the series $C^nH^{2n+2}$ and $C^nH^{2n}$, among the products obtained by distilling amylic alcohol with anhydrous chloride of zinc. The hydride of nonyl and nonylene occur in the portion of the distillate which goes over between 135° and 150°, and are separated by means of bromine, which combines with the nonylene (Wurtz, Bull. Soc. Chim. 1863, p. 300; Ann. Ch. Pharm. cxxviii. 225; Jahresb. 1863, p. 510). Hydride of nonyl is also contained, together with other alcoholic hydrides, in American petroleum (Pelouze and Cahours). See HYDRIDES, iii. 181.

Hydride of nonyl boils between 134° and 137°; its vapour-density by experiment is 4·50 (Wurtz); by calculation 4·432. Its odour is somewhat like that of lemons. (Pelouze and Cahours.)

*Chloride of Nonyl*, or *Chloride of Pelargyl*, $C^9H^{19}Cl$, obtained by the action of chlorine on hydride of nonyl, distils over as a colourless, mobile, aromatic liquid, having a specific gravity of 0·899 at 16°, and boiling at 196°. Heated with acetate of potassium to 150°, it yields *acetate of nonyl* as a liquid which has a fruity odour, boils between 208° and 212°, and when boiled with potash yields *hydrate of nonyl, nonylic* or *pelargonic alcohol*, as an oil boiling at about 200°. (Pelouze and Cahours.)

**NONYLAMINE.** $C^9H^{21}N$.—Obtained by the action of ammonia on chloride of nonyl. Colourless liquid having an aromatic and ammoniacal odour; boiling between 190° and 192°; somewhat soluble in water. (Pelouze and Cahours.)

**NONYLENE.** $C^9H^{18}$. *Pelargonene. Elaene.*—This hydrocarbon occurs, together with hexylene, among the products of the dry distillation of hydroleic or metoleic acid. The crude distillate is redistilled at 130° to remove a quantity of empyreumatic matter; the liquid which passes over is agitated with dilute potash-ley, to free it from volatile acids, and dried over chloride of calcium; and the hexylene and nonylene are finally separated by fractional distillation (Frémy, Ann. Ch. Phys. [2] lxv. 143). It is also found, together with hydride of nonyl, &c., among the products of the distillation of amylic alcohol with chloride of zinc (Wurtz, *loc. cit.*). It is a colourless liquid, lighter than water, insoluble in water, soluble in alcohol and ether; has a penetrating odour; burns with a bright white flame; boils at about 110° (Frémy); at about 140° (Wurtz). Vapour-density, obs. = 4·071—4·488 (Frémy); 4·54 (Wurtz); calc. = 4·359.

*Bromide of Nonylene*, $C^9H^{18}Br^2$, formed by direct combination, is a non-volatile liquid, which, like its congeners, is attacked by caustic potash, yielding a liquid boiling between 140° and 200°. (Wurtz.)

*Chloride of Nonylene*, $C^9H^{18}Cl^2$, also formed by direct combination at ordinary temperatures, is an oily liquid, heavier than water, having a rather agreeable odour much like that of anise; it burns with a green smoky flame. (Frémy.)

**NONYLIC ALCOHOL.** See NONYL (p. 134).

**NORDENSKIÖLDITE.** A mineral from Ruscula on Lake Onega in Russia, probably a variety of tremolite (iii. 169). Contains, according to C. v. Hauer, 60·78 per cent. silica, 2·63 ferric oxide and alumina, 14·12 lime, and 22·46 magnesia. (Jahresb. 1854, p. 820.)

**NORITE.** A rock occurring near Egersund and other places on the west coast of Norway. Its composition is that of a gabbro, somewhat poor in augitic constituents (hypersthene and diallage), and characterised in several places by an admixture of titaniferous iron. Kjerulf (Jahresb. 1862, p. 791), found in a norite from Tronfjeld in the Oesterthal, of grey to violet colour and containing labradorite and green diallage: 50·06 per cent. silica, 5·73 titanic oxide, 16·44 alumina, 9·71 ferric oxide, 14·66 lime, 4·88 magnesia, 1·38 soda and a trace of potash.

**NORIUM.** The name of a metal which has been supposed to accompany zirconium in most, if not all of the minerals which contain it. This idea of the composite nature of the earth commonly called zirconia, is based upon some experiments of Svanberg (Pogg. Ann. lxv. 317), who found that when chloride of zirconium was fractionally precipitated by oxalic acid, the several precipitates exhibited considerable differences of composition. On the other hand, Berlin (J. pr. Chem. lvii. 145) finds that the several precipitates of oxalate of zirconium thus produced do not exhibit any differences of composition sufficiently great to warrant such a conclusion. The matter requires therefore further investigation.

**NOSEAN.** A mineral allied to haüyne (iii. 15), occurring in rhombic dodecahedrons, sometimes modified with faces of the cube, more rarely of the trapezohedron 2 O 2; often granular massive. Hardness = 5·5. Specific gravity = 2·25—2·3. Colour greyish, bluish, or brownish, sometimes black. Translucent to nearly opaque. Before the blowpipe, it loses colour and fuses on the edges. Gelatinises with acids.

Nosean is found chiefly in the eruptive rocks at Lake Laach, near Andernach on the Rhine; also at Rieden and Volkerfeld in Prussia in a leucite rock.

The following are analyses of the mineral, mostly from Lake Laach:—*a*, *b*. Bergemann (Bull. de sc. nat. 1823, iii. 406).—*c*. Varrentrapp (Pogg. Ann. xlix. 515).—*d*. Whitney (*ibid.* lxx. 431).—*e*. Blackish-green to clove-brown; specific gravity 2·280.—*f*. Light bluish-grey; specific gravity 2·299.—*g*. Leek-green, from the Haardt near Rieden; specific gravity 2·336.—*h*. Transparent and colourless, mostly in twin-crystals (the so-called sodalite from Lake Laach); specific gravity 2·399 (G. v. Rath, Jahresb. 1863, p. 822):

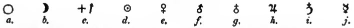
| | *a*. | *b*. | *c*. | *d*. | *e*. | *f*. | *g*. | *h*. |
|---|---|---|---|---|---|---|---|---|
| Silica | 38·50 | 37·00 | 35·99 | 36·52 | 36·72 | 36·69 | 36·46 | 36·87 |
| Sulphuric anhydride | 8·16 | 11·56 | 9·17 | 7·40 | 7·52 | 7·30 | 7·34 | 10·00 |
| Chlorine | . . | . . | 0·65 | 0·61 | 0·71 | 1·05 | 0·70 | 1·08 |
| Alumina | 29·25 | 27·50 | 32·56 | 29·48 | 29·08 | 28·45 | 29·61 | 26·60 |
| Ferric oxide (with manganic oxide) | 2·67 | 1·78 | 0·06 | 0·44 | 0·75 | 0·47 | 0·91 | 0·28 |
| Lime | 1·14 | 8·14 | 1·11 | 1·35 | 1·20 | 0·63 | 2·37 | 4·05 |
| Soda | 16·56 | 12·24 | 17·84 | 23·04 | 23·33 | 23·90 | 20·60 | 20·75 |
| Potash | . . | . . | . . | . . | 0·34 | . . | . . | trace |
| Water | . . | . . | 1·85 | 1·37 | 0·83 | 2·15 | 2·01 | 0·37 |
| Sulphur | 2·82 | 1·41 | | | | | | |
| | 99·10 | 99·63 | 99·23 | 100·21 | 100·48 | 100·64 | 100·00 | 100·00 |

Rammelsberg suggests as probable that nosean has the composition $(\text{NaCl}.3\text{NaAl}'''\text{SiO}^4) + 5(\text{Na}^2\text{SO}^4.6\text{NaAl}'''\text{SiO}^4)$, that is to say that it consists of 1 molecule of sodalite united with 5 molecules of a soda-haüyne containing 6 atoms of silicate. This formula requires 36·83 per cent. silica, 7·25 sulphuric anhydride, 30·71 alumina, 24·15 soda, and 1·06 chloride of sodium.

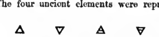
**NOTATION.** The system of chemical notation now in use among chemists belongs exclusively to modern times, for it is essentially an expression of the doctrine of definite combining proportions, and the atomic theory. But in all ages in which chemistry has been cultivated, signs of some kind or other seem to have been employed to represent the various kinds of matter; and although we may regard the definite quantitative value which chemical symbols have possessed since the introduction of the atomic theory, as constituting an essential difference between the chemical notation of the present day and that of any former age, still it is not difficult to trace, in the notations of the earlier periods of the science, nearly all the most important elements of that now employed.

The very early belief* in a connection between the several members of the solar system and individual metals led to the representation of both, not only by the same names (Nomenclature, p. 118), but by the same signs. The following account given by Hassenfratz and Adet of the appropriation by the early chemists of these signs to the particular metals, shows that they were by no means applied arbitrarily or at random, but in accordance with a general system of ideas. "The metals were divided into coloured or solar metals, and white or lunar metals. The metals of these two classes were again subdivided into perfect, semi-perfect, and imperfect metals; perfection was expressed by a circle, *a*, *fig.* 732; semi-perfection, if we may use such an expression, by a semi-circle, *b*; and imperfection by a cross or by a dart, *c*. Thus gold, which was preeminently the solar metal, was represented by a simple circle, *d*; this figure was common to the metals of the same class, as copper *e*, iron *f*, and antimony *g*; but for these it was combined with the symbol of imperfection. Silver, which they considered as a semi-perfect lunar metal, was denoted by a semi-circle *b*; tin, *h*, and lead, *i*, had likewise the semi-circle for their symbol, as belonging to the same class; but they were distinguished from silver by the cross or by the dart. Finally, mercury, which was an imperfect metal, at once solar and lunar, bore the distinctive marks of both these classes, and was denoted by a circle surmounted by a semi-circle with the addition of a cross, *j*." (*Mémoire sur de nouveaux caractères à employer en Chimie*, 1787.)

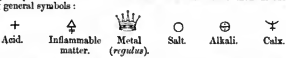
*Fig.* 732.



Additional symbols, framed by individual chemists in accordance with their own special opinions, were employed to denote other substances, but those given above long remained in universal use. We still find them among the chemical signs adopted by Bergman, whose system may be taken as the latest important representative of the ideas which reigned in chemistry before the time of Lavoisier, and is therefore entitled to a passing notice. The four ancient elements were represented by Bergman as follows:—



and the principal classes into which chemical substances were then divided, by the following general symbols:



In order to denote particular substances, one of these general symbols was used, in combination with some special sign of difference: thus the several acids were denoted by a cross followed by a sign characteristic of each; the metallic calces by the symbol "calx," (which when followed by the letter *p*, for *pura*, signified lime), followed by the special sign of some particular metal. (See Hassenfratz and Adet, *op. cit.*; also the frontispiece to "A Dissertation on Elective Attractions, by Torbern Bergman," London, 1785; and the plates to Pearson's "Translation of the Table of Chemical

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* Bergman quotes a passage from the writings of Celsus against Origen, according to which this belief existed among the ancient Persians.

Nomenclature proposed by **Guyton, Lavoisier, Bertholet,** and **De Fourcroy,**" 2nd edit. London, 1799. In the last work the signs employed by **Geoffroy** will also be found; for information on the origin of chemical symbols, the author refers to a "Tract on Symbols," by Wall of Oxford, written in 1783).

These signs of Bergman's, and indeed all that had hitherto been employed, indicated the substances to which they were applied, exactly in the same way as the ordinary names of those substances indicated them. They may in fact be regarded as merely abbreviated modes of writing chemical names, for the information which they conveyed was precisely the same as that given by the latter. These symbols did not express, and had not any necessary relation to the composition of the substances they denoted; and indeed it is evident that at a period when fire, air, earth, and water were still regarded as the elements of all material things, chemists can have had no clear ideas to express touching what is now understood by chemical composition. Accordingly, we first find chemical signs used in their modern sense, that is, to denote chemical composition, by the philosopher who first clearly pointed out what was to be understood thereby. In a memoir by **Lavoisier**, entitled, "Considérations générales sur la dissolution des Métaux dans les acides," published in the Mémoires de l'Académie des Sciences (année 1782, p. 492; also "Œuvres de Lavoisier," ii. 509. 4to, Paris 1862), occurs probably the first example of the employment of symbols to denote the successive steps of a chemical operation. The meaning which Lavoisier attached to the signs used by him will be best conveyed in his own words.

" . . . . j'ai construit des espèces de formules qu'on pourrait prendre d'abord pour des formules algébriques, mais qui n'ont point le même objet, et qui ne dérivent point des mêmes principes; nous sommes encore bien loin de pouvoir porter dans la chimie la précision mathématique, et je prie en conséquence de ne considérer les formules que je vais donner que comme des simples annotations, dont l'objet est de soulager les opérations de l'esprit.

| | |
|---|---|
| Soit une substance métallique quelconque . . . . . | *S.M.* |
| Un acide quelconque . . . . . . . . . . | ⌒ |
| L'eau . . . . . . . . . . . . | ▽ |
| Le principe oxygine . . . . . . . . . . | ⊕ |
| L'air nitreux . . . . . . . . . . . | △ǂ |
| L'acide nitreux . . . . . . . . . . . | ⊖ǂ |

"On aura, pour expression générale de toute dissolution métallique,

(*S.M.*) (▽ ⌒).

"Cette formule générale variera suivant la nature de l'acide et suivant celle du métal; ainsi, par exemple, si c'est la dissolution du fer dans l'acide nitreux qu'on veut exprimer, on aura (♂) (▽ ⊖ǂ).

"Mais l'acide nitreux étant lui-même un composé, il faut, dans cette formule, y substituer sa valeur, et alors la formule prendra la forme qui suit (♂) (▽ ⊕ △ǂ).

"Soit supposé la quantité de fer $= a$, il est clair qu'il faudra, pour dissoudre une quantité $a$ de fer, une quantité déterminée d'acide; qu'il y a, par conséquent, une relation entre la quantité d'acide et celle du fer; et qu'en nommant $b$ cette relation, j'aurai $a\,b$ pour l'expression de la quantité d'acide nécessaire à la dissolution.

"Il est clair encore qu'une quantité $a\,b$ d'acide nitreux est composée d'une certaine portion d'eau, que je pourrai nommer . . . . . . . . $\frac{ab}{q}$

"D'une certaine portion de principe oxygine, que je pourrai nommer . $\frac{ab}{s}$

"D'une certaine portion d'air nitreux que je pourrai nommer . . . $\frac{ab}{t}$

"Enfin je ferai observer que, pour que ces sortes de dissolutions ne se fassent pas d'une manière trop tumultueuse, il est nécessaire de couper l'acide de deux parties d'eau, d'après quoi la formule ci-dessus deviendra:

$$(a \text{♂}) + (2ab \triangledown + \frac{ab}{q} \triangledown) + (\frac{ab}{s} \oplus + \frac{ab}{t} \text{△ǂ}).$$

"Telle est la formule qui représente l'expression du dissolvant et de la substance à dissoudre avant le mélange. Mais sitôt que l'action dissolvante a lieu, le métal enlève à l'acide nitreux la quantité de principe oxygine nécessaire pour se saturer. Cette quantité est encore, pour chaque métal, dans un rapport constant avec la quantité de ce même métal, et, puisque j'ai nommé $a$ la quantité du métal, je pourrai nommer

$\frac{a}{p}$ la quantité de principe oxygine nécessaire pour le saturer. Il est clair que, quand la dissolution est faite, cette quantité doit être ajoutée au fer dans la formule, et retranchée de l'expression de l'acide nitreux; ainsi la formule deviendra:

$$(a\,\text{♂} + \frac{a}{p}\oplus) + (2ab\,\nabla + \frac{ab}{q}\,\nabla) + (\frac{ab}{s}\oplus - \frac{a}{p}\oplus + \frac{ab}{t}\triangle\!\!+).$$

Et, à cause qu'il se dégage de la combinaison une quantité d'air nitreux à peu près égale en poids à celle de principe oxygine absorbée par le métal, il faut retrancher $\frac{a}{p}\triangle\!\!+$ de cette formule pour avoir l'expression réelle de ce qui restera après la dissolution; on aura:

$$(a\,\text{♂} + \frac{a}{p}\oplus) + (2ab\,\nabla + \frac{ab}{q}\,\triangle) + (\frac{ab}{s}\oplus - \frac{a}{p}\oplus + \frac{ab}{t}\triangle\!\!+ - \frac{a}{p}\triangle\!\!+).$$

"Les parenthèses expriment la manière dont sont groupées les molécules de différente nature dans la dissolution.

"Pour plus de simplification, je supposerai que, dans toutes ces dissolutions, la quantité d'acide employée est toujours d'une livre; d'après quoi, $a\,b$ deviendra égal à l'unité, et la formule se réduira à ce qui suit:

$$(a\,\text{♂} + \frac{a}{p}\oplus) + (2\,\nabla + \frac{1}{q}\,\nabla) + (\frac{1}{s}\oplus - \frac{a}{p}\oplus + \frac{1}{t}\triangle\!\!+ - \frac{a}{p}\triangle\!\!+).$$

"Il ne s'agit plus que de donner une valeur numéraire à toutes ces quantités; et je vais rendre compte des principales expériences dont je suis parti."

In the remainder of this paper, Lavoisier compares the numerical results calculated by means of this formula with those yielded by actual experiment, and shows how similar formulæ may be applied in other cases.

Although the notation employed by Lavoisier, in the memoir from which we have quoted, was distinctly founded upon the principle of denoting compound bodies by means of their elementary constituents, this principle was nevertheless only very imperfectly carried out, water for instance being still represented by Bergman's symbol instead of by the symbols of its elements, notwithstanding that Lavoisier had himself published in the previous year two memoirs demonstrating its compound nature. But the rapid advances in systematisation which took place in the next few years, soon rendered it possible to apply this most important principle in a much more complete manner. Accordingly, in 1787, Hassenfratz and Adet published two memoirs (from one of which we have already quoted, p. 136), wherein they proposed a much more complete and systematic chemical notation than any that had hitherto been proposed. They began by assigning symbols to the elementary or undecompounded bodies, employing similar symbols for all the bodies of the same class, and giving the simplest to such as were of most frequent occurrence. Thus, caloric, oxygen, and nitrogen were classed together as "substances which can exist in the aëriform condition at the ordinary temperature of the atmosphere, and which, as entering into the composition of an infinity of bodies, require the utmost simplicity in their characters," and were accordingly represented by different positions of a straight line: thus, | *caloric*, — *oxygen*, / *nitrogen*. The fourth position, \ was reserved to denote a new element of the same class whenever such might be discovered; and by adopting zigzag instead of straight lines, four additional symbols were obtained for bodies of the same class, one of them, $\wr$, being employed for *light*, and the three remaining positions being reserved "*pour designer de nouvelles substances simples et aëriformes lorsque l'on en decouvrira.*" Similarly, a semi-circle was used as the general symbol for combustible elements, each individual being distinguished by a particular position of the common character: thus ) *hydrogen*, ( *carbon*, ◡ *sulphur*, ◠ *phosphorus*. The other general symbols were as follows: △ *alkalis*, ▽ *earths*, ○ *metals*, □ *acidifiable compound radicles*, ◇ *non-acidifiable compound substances* (such as *ether*, *alcohol*, *oil*, &c.). These symbols not admitting of the formation of a sufficient number of special signs by mere variations of position, the signs representing particular substances were obtained by placing the initial letters of their names inside the common symbol of the class to which they belonged. For instance, among the metals, gold alone was denoted by the symbol ⊙, "in order," as the authors say, "to preserve the ancient character," the remainder being denoted by a circle, inside which was inscribed a letter, or in case of the names of more than one metal having the same initial, two letters, taken from their latin names. For instance, Ⓟ *lead*, Ⓨ *platinum*, Ⓐ *silver*, $\textcircled{\scriptsize As}$ *arsenic*, $\textcircled{\scriptsize St}$ *antimony*,

&c. Compound bodies were denoted by the juxtaposition of the symbols of their elements, these being placed upon the same horizontal line when the elements were regarded as mutually saturated, but when any element was supposed to be in excess, its symbol was placed below the line, or above if it was in defect. Thus represented *ice;* the same combined with a small quantity of caloric constituted *water* , and with caloric in excess it constituted *steam* .*

A most important alteration in the meaning of chemical symbols resulted from the introduction of the atomic theory; from this time they had not merely a qualitative but a quantitative signification, the symbol of each substance no longer representing an indefinite quantity of that substance, but a particular weight proportional to the supposed weight of its atom. The atomic symbols employed by **Dalton** had all the same general form, namely that of a circle, this form being most likely adopted by him because he considered the atoms themselves as in all probability spherical. Examples of some of the symbols employed by him for non-metallic elements have already been given in the articles ATOMIC WEIGHTS (i. 453) and EQUIVALENTS (ii. 494); in order to denote the several metals, he adopted the same expedient as Hassenfratz and Adet, namely placing their initial letters inside the circle.

In 1815, Berzelius proposed a system of notation in which the use of initial letters was extended to all the elements, and the use of the enclosing circles was dispensed with. At the same time he introduced the method of denoting several atoms of the same element, or several molecules of the same compound, by means of coefficients, thus bringing chemical notation almost exactly into its present state. But in addition to the modern system of chemical formulæ, which will be found more fully described below, Berzelius proposed a system of mineralogical formulæ, which though seldom met with in modern works, require some notice in a historical summary. These formulæ were used only for the alkaline, earthy and some metallic silicates. Silica and the various oxides occurring in these minerals were denoted by their initial letters, the higher (or -ic) oxides by capitals, and the lower (or -ous) oxides by small letters, italics being employed for both in order that these might not be confounded with the chemical formulæ. For instance, $K$ = potash. $N$ = soda, $B$ = baryta, $Sr$ = strontia, $C$ = lime, $A$ = alumina, $S$ = silica, $Mn$ = manganic oxide, $mn$ = manganous oxide, $F$ = ferric oxide, $f$ = ferrous oxide. When two symbols were joined without a coefficient, they represented a compound of two oxides in such proportion that each contained the same quantity of oxygen: thus (taking $S = SiO^3$), $AS$ stood for $Al^2O^3.SiO^3$; but when a coefficient was used, it denoted combination according to a multiple of the above proportion, as $AS^3 = Al^2O^3.3SiO^3$, or $A^2S = 2Al^2O^3.SiO^3$. (**Berzelius**, *Lehrbuch der Chemie*, ed. 1831, vol. iv. pt. 2, p. 1078.)

Still another system of abbreviated formulæ proposed by Berzelius is now seldom used, except by mineralogists, and may therefore be mentioned here in connexion with the foregoing. We refer to the use of dots placed above the symbol of an element in order to express its combination with oxygen, as $\ddot{S}$ for $SO^2$ and $\dddot{S}$ for $SO^3$. After the discovery of the sulphur-salts, this mode of notation was extended by the use of commas to stand for sulphur, short horizontal strokes for selenium, and small crosses for tellurium: thus

$\dot{K}\,\dddot{Mo}$ molybdate of potassium.

$\overset{,}{K}\,\overset{,,,}{Mo}$ sulpho-molybdate of potasssium.

$\overset{-}{K}\,\overset{---}{Mo}$ seleno-molybdate of potassium.

$\overset{+}{K}\,\overset{+++}{Mo}$ telluro-molybdate of potassium.

From a chemical point of view, these formulæ are open to the serious objection that they seem to imply an essential difference between the mode of combination of oxygen and its analogues, and that of all other elements. Accordingly, **Liebig** and **Poggendorf**, in their great Dictionary of Chemistry, recommended the entire abandonment of them (see *Handwörterbuch der reinen und angewandten Chemie*, preface to first edition; also Ann. Pharm. ix. 3, foot-note), as well as of the horizontal strokes through symbols used by Berzelius to denote double atoms. At the same time they proposed another modification of Berzelius's notation, which, though it has been extensively adopted, cannot be considered as an important improvement. This was the placing of the small numerals employed to multiply the elementary symbols, below the symbols instead of above them, as $CO_2$ instead of $CO^2$, $C_4H_8$ instead of $\cancel{C}^2H^4$ &c. The object of this latter alteration was to prevent the possibility of the coefficients employed in chemical formulæ being supposed to have the same meaning as the similarly placed exponents in mathematical formulæ. Mitscherlich, with the same object, avoided the use of the small numerals altogether; thus for instance he wrote chloride of benzoyl (using the atomic weights of the period) 14C10H2O2Cl instead of $C^{14}H^{10}O^2Cl^2$. The danger to be avoided was not however so great as to necessitate either of these expedients.

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* It is worthy of remark that, although we now know the conception of caloric as a substance to have been erroneous, the attempt to express the quantity of it contained in a material substance in any given state, rendered Hassenfratz and Adet's formulæ in one respect more complete than those now employed. The only similar attempt we are acquainted with in modern chemistry is the late Mr. Bowman's method of denoting the state of aggregation of a substance by varying the kind of type employed in printing its symbols. (See his *Practical Chemistry*, London 1818, pp. xviii.—xxiii.)

At first, even after they had assumed almost completely their modern form, chemical formulæ were not so much used to express processes of chemical change, as to denote the composition of individual substances. When they were used to express a reaction the arrangement of the symbols was usually different from that now commonly adopted. As a general rule, instead of a chemical equation as now written, the formulæ of the reagents were written one under the other, the similar atoms being added together, and the same was done with the formulæ of the products, and the sign = was placed between the two sums. For example, the transformation of prussic acid and water into formic acid ammonia is thus represented in Liebig's treatise on Organic Chemistry:

$$\left.\begin{array}{ll}\text{“ 1 equiv. of hydrocyanic acid,} & N^2C^2H^2 \\ \text{3 equiv. of water} \quad . \quad . & \qquad\quad H^6O^3 \\ \hline & N^2C^2H^8O^3\end{array}\right\} = \left\{\begin{array}{ll}\text{1 equiv. of ammonia} \quad . & N^2 \quad H^6 \\ \text{1 equiv. of formic acid} \ . & \quad C^2H^2O^3 \\ \hline & N^2C^2H^8O^3\text{.”}\end{array}\right.$$

But the more modern form of chemical equation with the sign + was likewise used not unfrequently, the idea of expressing chemical changes in this way dating in fact from Lavoisier, in whose *Traité élémentaire de Chimie* (Partie, i. chap. xiii.) there occurs a true chemical equation: namely,

“*Moût de raisin* = *acide carbonique* + *alcool.*”

Turner, Johnston, and Graham were among the first British chemists who adopted Berzelius's notation, and the earliest English elementary work into which it was introduced was the third edition of Turner's *Elements of Chemistry*. For some time, however, the use of the symbolic notation met with considerable opposition in this country, a certain number of chemists, one of the most considerable of whom was Richard Phillips, objecting to the system as a whole; while in other quarters objection was taken to the use of mathematical signs in a sense somewhat different from that which they bore in mathematics. Dr. Whewell, who was one of the most strenuous opponents of Berzelius's notation upon this ground, endeavoured to replace it by a system in which the mathematical meaning of the signs was more closely adhered to. But whatever may have been the merits of Whewell's notation, it was so far from corresponding to the actual requirements of chemical science, that it never came into use, and it is sufficient here to have referred to it.

[For particulars of the controversy above alluded to, see Whewell, *On the employment of Notation in Chemistry*, Journ. Roy. Inst., i. 347, May 1831.—Prideaux, *Reply to Whewell, advocating Berzelius's System*, Phil. Mag. Ann. N. S. x. 104, Aug. 1831.—Warington, *On Chemical Symbols*, with remarks on Whewell's paper, Phil. Mag. Journ. i. 181.—Berzelius, *Reply to Whewell*, Jahresb. xv. 201.—Whewell, *Reply to Berzelius*, Phil. Mag. Journ. iv. 9.—R. Phillips, *On the use of Chemical Symbols*, ibid. iii. 443; iv. 246.—Prideaux, *Replies to Phillips*, ibid. iv. 41; 464.—Graham, *Replies to Phillips*, ibid. iv. 106; 402.—Whewell's system of notation may also be found in Brande's *Manual of Chemistry*, 5th edit. 1841.]

The important modifications or extensions which the notation of chemistry has received since the time of Berzelius, are not numerous. Among the most valuable we may mention the introduction, by Gerhardt, of “general formulæ,” in which letters of variable value are used as coefficients instead of numbers, and Odling's method of denoting the atomicity of polyatomic elements and radicles by means of accents placed above their symbols. (Chem. Soc. Qu. J. vii. 1.)

The consideration of the quantitative value of the symbols of the elements does not come within the scope of this article, and has moreover been fully discussed in previous articles to which we must refer (ATOMIC WEIGHTS, i. 452; EQUIVALENTS, ii. 491; METALS, ATOMIC WEIGHTS AND CLASSIFICATION OF, iii. 957). The various opinions that have been held of late years in relation to this subject, have however introduced a good deal of confusion into chemical notation, and have caused the more or less general adoption of a variety of expedients for avoiding the consequent ambiguity. Such of these as are employed in the present work are explained below.

It now only remains to explain the rules which are generally followed by the leading chemists of the present day with respect to chemical notation, and especially those which are adopted in this work. The symbols employed to represent atomic proportions of the several elementary bodies, form the basis of this notation. A table of these symbols, and of their numerical values, has already been given at pages 464 and 465 of vol i.; we may therefore assume that they are known. Compound bodies are represented by the juxtaposition of the symbols of the elementary atoms which enter into the composition of one molecule. A single atom is represented in the formula of a compound, by the corresponding symbol without any addition; two or more atoms are represented, either by a repetition of the symbol, or by placing after it a small numeral, above or below the line. For example, the formula CHNO represents cyanic acid, one molecule of which contains one atom of carbon, one atom of hydrogen, one atom of nitrogen, and one atom of oxygen; HHO, or $H^2O$, or $H_2O$, represents the compound of 2 at. hydrogen with 1 at. oxygen; $C^2H^4N^2O^2$ represents a molecule of oxamide containing 2 at. carbon, 4 at. hydrogen, 2 at. nitrogen, and 2 at. oxygen. Sometimes it is required to represent the fact that in some particular reaction, or set of reactions, certain atoms of a compound act differently from the remainder: in such a case the symbols of the atoms in question are usually inclosed within brackets, a numeral being added outside when needful, which then multiplies all the symbols contained between the brackets. For instance, in order to express that in monethylic succinate the group of atoms $C^2H^5$ behaves in many reactions differently from the rest, the formula of the compound may be written $C^4H^5(C^2H^5)O^4$, instead of $C^6H^{10}O^4$; similarly, diethylic succinate may be written thus, $C^4H^4(C^2H^5)^2O^4$, instead of $C^8H^{14}O^4$. If for any reason it is desired to call special attention to certain symbols which are already contained within brackets together with others, this may be done by placing a *vinculum* over them, or by putting them between round brackets, and the larger bracketed group of which they form part between square brackets. Thus, suppose we want to write the formula of ethylic dichloracetate in such a manner as to call attention at once to the particular functions of the groups constituting the radicles ethyl and dichloracetyl, and to the fact that the number of chlorine and hydrogen-atoms in dichloracetyl is equal to the number of hydrogen atoms in acetyl—this may be done in one of the following ways:

$$(C^2\overline{HCl^2}O)(C^2H^5)O, \text{ or } [C^2(HCl^2)O](C^2H^5)O.$$

Another method of pointing out the relation between substitution-derivatives and the corresponding normal compounds, is to place the symbols of the substituting atoms at the same part of the formula as would otherwise have been occupied by the symbols of the atoms whose place they have taken, writing them when needful above or below the line. For example, nitrobenzoic acid may be represented thus, $C^7\begin{matrix}NO^2\\H^5\end{matrix}O^2$, to express the fact that the atoms $NO^2$ have taken the place occupied by an atom of hydrogen in the normal compound $C^7H^6O^2$; similarly, dibromo-trichloro-naphthalene may be written $C^{10}\begin{matrix}Br^2\\Cl^3\\H^2\end{matrix}$. This mode of arranging symbols in a formula is especially used to represent the constitution of bodies which may be conceived as formed by the substitution of other atoms or radicles for hydrogen in the typical compounds HCl, $H^2O$, $H^3N$, &c.; *e.g.* ethylic acetate when compared to the type $H^2O$ is often written $\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}O$ or $\left.\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}\right\}O$; similarly diethylamine, when compared to the type $H^3N$, is often written $\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}N$ or $\begin{matrix}(C^2H^5)^2\\H\end{matrix}N$ or $\left.\begin{matrix}(C^2H^5)^2\\H\end{matrix}\right\}N$, &c. In order to facilitate comparison, the formulæ of the primitive types are often written in the same manner; as water $\begin{matrix}H\\H\end{matrix}O$ or $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, ammonia $\begin{matrix}H\\H\\H\end{matrix}N$ or $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$. The use of a brace $\}$ in such formulæ has no other object than to indicate a little more clearly the exact relative positions of the symbols, and thereby the supposed order of combination of the atoms they represent.

In order to represent chemical changes by means of symbols, the formulæ of the reacting bodies are written on one side of an equation, and the formulæ of the products on the other, the several terms on each side being separated by the sign +, as—

$$NKO^3 + SH^2O^4 = NHO^3 + SHKO^4;$$

or, if it is desired to direct special attention to some one product, this is placed alone on one side of the equation, as

$$NHO^3 + KHO - H^2O = NKO^3.$$

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With regard to the meaning of the algebraic signs =, + and − in chemical equations, it must be observed that the sign = expresses merely *equality in weight;* the sign +, that two substances between whose formulæ it is placed are *mixed together;* and the sign −, the *separation* or *removal* from each other of two substances. Sometimes however we meet with the sign + used to denote combination; but such an employment of it is apt to lead to great confusion and ought always to be avoided.

If two or more molecules take part in or result from a reaction, the number of molecules is expressed by a full-sized numeral preceding the formula of the substance in question: thus when chlorine is prepared by heating a mixture of chloride of sodium, manganic dioxide, and sulphuric acid, the reaction takes place between two molecules of the chloride, one molecule of the oxide, and two molecules of the acid, and is consequently represented by an equation thus—

$$2NaCl + Mn^2O^2 + 2H^2SO^4 = Na^2SO^4 + Mn^2SO^4 + 2H^2O + Cl^2.$$

The manner in which the large and small numerals are employed in chemical formulæ will be easily understood, if it is borne in mind that the use of the former is to multiply the formulæ of molecules, while that of the latter is to multiply the symbols of atoms, or the formulæ of radicles behaving like atoms. Sometimes these coefficients are interchanged, but this is always incorrect, as their true meaning is quite distinct, for instance the formula $C^4H^8$ cannot have the same meaning as $2C^2H^4$; similarly two molecules of water ought always to be written $2H^2O$, not $H^4O^2$, which would, strictly speaking, be the formula of a compound one molecule of which contained four atoms of hydrogen and two atoms of oxygen. A similar remark applies to small numerals employed to multiply a group of symbols inclosed within brackets: *e.g.* $(C^2H^3O)^2$ should not be written $(C^4H^6O^2)$ nor *vice versâ.* When the formula to be multiplied by prefixing a large numeral is already broken up, by some of the symbols being contained within brackets or otherwise, it is well, in order to avoid possible misconception, to inclose the whole formula again in brackets, putting the numeral outside. Thus, if the formula of two molecules of alcohol were written $2(C^2H^5)HO$, the 2 might be supposed to multiply only the symbols between the brackets: to avoid any ambiguity it would be better to write $2[(C^2H^5)HO]$.

Sometimes the symbols making up the formula of a single molecule are separated by a *point,* as $Na^2SO^4.10H^2O$. The proper meaning of this sign is to denote that if the atoms represented by the symbols on either side of it are removed, one or more complete molecules will still be left. When a numerical coefficient is prefixed to such a formula, its multiplying power extends only to the symbols preceding the point: thus the formula $2KCl.SbCl^3$ is not equivalent to $2(KCl.SbCl^3)$. When the numeral is intended to apply to the whole formula, this should *always* be placed within brackets.

In the application of chemical formulæ to mineralogy, it is often needful to be able to represent the general composition of a mineral, the composition of particular specimens of which may vary considerably, in consequence of the more or less complete replacement of one constituent by one or more others, isomorphous with it. Thus the formula of normal orthoclase or potash-felspar is $KAl^2Si^3O^8$, but the composition of the mineral often differs considerably from that represented by this formula, the potassium being partially replaced by an equivalent quantity of sodium, magnesium, or calcium, and the aluminium partially replaced by iron. This variability of composition is expressed by writing the formula thus:

$$(K;\ Na;\ Mg;\ Ca)(Al;\ Fe)^2Si^3O^8,$$

which signifies that each molecule contains a quantity of potassium, sodium, magnesium, and calcium which is together equivalent to one atom of potassium, and a quantity of aluminium and iron which is altogether equivalent to two atoms of aluminium.

The symbols given in the table already referred to (i. 464, 465) represent in nearly all cases the atomic weights adopted by Gerhardt; but in addition to these, other scales of atomic weights are in use which it is often needful to distinguish by the employment of different symbols. In the first place, there is the scale adopted in "Gmelin's Handbook of Chemistry," and some years ago almost universally employed in this country: when formulæ founded upon this scale are used in this work, they are distinguished by being printed in italics. Secondly, in order to denote atomic weights twice as great as those assumed by Gerhardt, the ordinary symbol is changed by the reduplication of its first consonant, as Ppb, Ffe, All, &c., or a horizontal stroke is drawn through it, as Ᵽb, Ꞙe, Ⱥl, &c. These modes of notation are not employed precisely in the same way by all chemists, but as special methods are seldom adopted without the necessary explanations being given at the same time, we need not enter into further detail. It is greatly to be desired that all chemists should agree in regarding the modified notations now in use, as merely temporary expedients, and that they should aim at returning as soon as practicable to the uniform and sole use of the symbols originally proposed by Berzelius.

G. C. F.

**NOTITE.** Palagonite from Val de Noto.

**NUCIN.** A substance contained in green walnut-shells. It is prepared by mixing the ethereal extract of the shells with a perfectly neutral solution of cupric sulphate till it assumes a pure blood-red colour; then decanting and filtering, and cautiously adding nitric acid (avoiding an excess) till the red colour changes to blue-green. The nucin is thereby set free, and by dissolving it in ether and evaporating over oil of vitriol, may be obtained in the form of a yellow powder composed of microscopic needles. It is insoluble in water, sparingly soluble in alcohol, sublimes at a little above 100° (or according to later experiments, somewhat below 90°), in reddish-yellow needles. Ammonia, fixed alkalis, and salts having an alkaline reaction, impart to it a splendid red colour. The red ammoniacal solution mixed with hydrochloric acid deposits a brown-red flocculent precipitate, soluble with red colour in ammonia. Nucin is free from nitrogen, but its exact composition has not been determined. (Vogel and Reischauer, Jahresb. 1856, p. 693; 1858, p. 533.)

The name *Nucin* has also been applied to a brown resinous substance found by Brandes in the hard shell of the cocoa-nut.

**NUCLEIN.** A name applied, sometimes to the albuminous constituent of the crystalline lens (*Handwörterbuch*, v. 623), sometimes to the substance forming the nucleus of the blood-cells. (*Lehmann's Physiological Chemistry*, ii. 186.)

**NUCLEUS THEORY.** *Théorie des Noyaux. Kerntheorie.*—A theory of the constitution of organic compounds, devised by Laurent (Ann. Ch. Phys. [2] lxi. 125), and adopted, with some modifications, by Leopold Gmelin in his "Handbook of Chemistry," (English edition, vol. vii. p. 18). It supposes all organic compounds to be formed from certain hydrocarbons containing even numbers of carbon and hydrogen-atoms,* *e. g.* Ethylene $C^4H^4$, Amylene $C^{10}H^{10}$, Benzene $C^{12}H^6$, Naphthalene $C^{20}H^8$. These are called Primary Nuclei; and from them are formed Secondary Nuclei by substitution of chlorine, bromine, oxygen, sulphur, nitryl ($NO^4$), amidogen ($NH^2$), &c. for equivalent quantities of hydrogen, *e. g.* from naphthalene the secondary nuclei, $C^{20}H^7O$, $C^{20}H^6Br^2$, $C^{20}H^5Cl^3$, $C^{20}H^6(NO^4)^2$, &c., &c. Further, both primary and secondary nuclei are capable of attaching to themselves externally, as it were, certain atoms or groups of atoms, always in even numbers, thereby producing alcohols, ethers, acids, alkaloïds, &c., &c. Thus ethylene, $C^4H^4$, by addition of the group HO, produces ether, $C^4H^4.HO = C^4H^5O$; with $H^2O^2$ it forms alcohol, $C^4H^4.H^2O^2 = C^4H^6O^2$; with $O^2$, aldehyde; with $O^4$, acetic acid, &c.; again, from the secondary nucleus dioxethylene, $C^4H^2O^2$, is formed oxalic acid, $C^4H^2O^2.O^6 = C^4H^2O^8$; trichlorethylene, $C^4Cl^3H$, with $O^2$ forms chloral, $C^4Cl^3H.O^2$;—amidethylene, $C^4(NH^2)H^3$ or $C^4AdH^3$, yields acetamide, $C^4AdH^3.O^2 = C^4H^5NO^2$, and ethylamine, $C^4AdH^3.H^2 = C^4H^7N$, &c.

Lastly, the compounds thus formed are capable of uniting with others both organic and inorganic, forming what are called conjugated compounds, including the so-called compound ethers, conjugated acids, &c.

Thus, in the ethylene series, we have neutral ethylic phosphate, $3C^4H^5O.PO^5$; ethylic biborate, $C^4H^5O.2BO^3$; ethyl-sulphuric acid, $C^4H^6O^2.2SO^3$; xanthic acid, $C^4H^6O^2.2CS^2$; bichlorocarbonic ether, $C^4Cl^2H^3O.CO^2$; perchloro-carbonic ether, $C^4Cl^5O.CO^2$; terchlorethylic acetate, $C^4Cl^3H^2O.C^4H^3O^3$; carbamic ether or urethane, $C^4AdH^3.2CO^2$; taurine, $C^4AdH^3.2SO^2$, &c.

As a further illustration, we give the entire series of compounds derived from the amylene, $C^{10}H^{10}$ (Handbook, vol. xi.).

PRIMARY NUCLEUS, $C^{10}H^{10}$.

Amylene, $C^{10}H^{10}$
Amylic Hydride, $C^{10}H^{10}.H^2$
Amylic Ether, $C^{10}H^{10}.HO$
Amylic Alcohol, $C^{10}H^{10}.H^2O^2$
Valeraldide, $C^{10}H^{10}.O^2$
Valerianic acid, $C^{10}H^{10}.O^4$

Amylic Sulphide, $C^{10}H^{10}.HS$
Amylic Mercaptan, $C^{10}H^{10}.H^2S^2$
Amylic Iodide, $C^{10}H^{10}.HI$
Amylic Bromide, $C^{10}H^{10}.HBr$
Amylic Chloride, $C^{10}H^{10}.HCl$
Telluramyl, $C^{10}H^{10}.HTe$

*Conjugated Compounds of the Primary Nucleus,* $C^{10}H^{12}$.

| | | | |
|---|---|---|---|
| Amylic Carbonate . . | $C^{10}H^{11}CO^3$ | = | $C^{10}H^{11}O.CO^2$ |
| Tribasic Amylic Borate . | $C^{30}H^{33}BO^6$ | = | $3C^{10}H^{11}O.BO^3$ |
| Amylic Biborate . . | $C^{10}H^{11}B^2O^7$ | = | $C^{10}H^{11}O.2BO^3$ |
| Amylic Phosphite . . | $C^{20}H^{23}PO^6$ | = | $2C^{10}H^{11}O.PHO^4$ |
| Amylophosphorous acid . | $C^{10}H^{13}PO^6$ | = | $C^{10}H^{12}O^2.PHO^4$ |

---

* The symbols used in this article have the same values as in Gmelin's Handbook; H = 1, C = 6, O = 8, S = 16, &c.

*Conjugated Compounds (continued).*

| | | | |
|---|---|---|---|
| Amylophosphoric acid | $C^{10}H^{13}PO^{8}$ | = | $C^{10}H^{12}O^{2}.PHO^{6}$ |
| Amylosulphurous acid | $C^{10}H^{12}S^{2}O^{6}$ | = | $C^{10}H^{12}O^{2}.2SO^{2}$ |
| Amylosulphuric acid | $C^{10}H^{12}S^{2}O^{8}$ | = | $C^{10}H^{12}O^{2}.2SO^{3}$ |
| Amylxanthic acid | $C^{12}H^{12}O^{2}S^{4}$ | = | $C^{10}H^{12}O^{2}.2CS^{2}O$ |
| Methylamylic Oxysulphocarbonate | $C^{14}H^{14}O^{2}S^{4}$ | = | $C^{10}H^{11}(C^{2}H^{3})O^{2}.2CS^{2}$ |
| Ethyl-amylic Oxysulphocarbonate | $C^{16}H^{16}O^{2}S^{4}$ | = | $C^{10}H^{11}(C^{4}H^{5})O^{2}.2CS^{2}$ |
| Amylic Dioxysulphocarbonate | $C^{12}H^{11}O^{2}S^{4}$ | = | $C^{10}H^{11}O^{2}C.^{2}S^{4}O$ |
| Amylic Nitrite | $C^{10}H^{11}NO^{4}$ | = | $C^{10}H^{11}O.NO^{3}$ |
| Amylic Nitrate | $C^{10}H^{11}NO^{6}$ | = | $C^{10}H^{11}O.NO^{5}$ |
| Bibasic Silicate of Amyl | $C^{20}H^{22}SiO^{4}$ | = | $2C^{10}H^{11}O.SiO^{2}$ |
| Amylic Formate | $C^{12}H^{12}O^{4}$ | = | $C^{10}H^{11}O.C^{2}HO^{3}$ |
| Amylic Chloroformate | $C^{12}H^{11}ClO^{4}$ | = | $C^{10}H^{11}O.C^{2}ClO^{3}$ |
| Methylic Valerate | $C^{12}H^{12}O^{4}$ | = | $C^{2}H^{3}O.C^{10}H^{9}O^{3}$ |
| Amylic Cyanide | $C^{12}NH^{11}$ | = | $C^{10}H^{10}.C^{2}NH$ |
| Amylic Sulphocyanide | $C^{12}NH^{11}S^{2}$ | = | $C^{10}H^{10}.C^{2}NHS^{2}$ |
| Amylic Acetate | $C^{14}H^{14}O^{4}$ | = | $C^{10}H^{11}O.C^{4}H^{3}O^{3}$ |
| Amylic Chloracetate | $C^{14}Cl^{2}H^{12}O^{4}$ | = | $C^{10}H^{11}O.C^{4}Cl^{2}HO^{3}$ |
| Ethylic Valerate | $C^{14}H^{14}O^{4}$ | = | $C^{4}H^{5}O.C^{10}H^{9}O^{3}$ |
| Amylic Oxalate | $C^{24}H^{22}O^{8}$ | = | $2C^{10}H^{11}O.C^{4}O^{6}$ |
| Amyloxalic acid | $C^{14}H^{12}O^{8}$ | = | $C^{10}H^{12}O^{2}.C^{4}O^{6}$ |
| Monovalerin | $C^{16}H^{16}O^{8}$ | = | $C^{6}H^{8}O^{6}.C^{10}H^{8}O^{2}$ |
| Bivalerin | $C^{26}H^{24}O^{10}$ | = | $C^{6}H^{8}O^{6}.(C^{10}H^{8}O^{2})^{2}$ |
| Trivalerin | $C^{36}H^{32}O^{12}$ | = | $C^{6}H^{8}O^{6}.(C^{10}H^{8}O^{2})^{3}$ |
| Valerone | $C^{18}H^{18}O^{2}$ | = | $C^{10}H^{10}O^{2}.C^{8}H^{8}$ |
| Valeracetone | $C^{12}H^{12}O^{2}$ | = | $C^{10}H^{10}O^{2}.C^{2}H^{2}$. |
| Amylomalic acid | $C^{16}H^{16}O^{10}$ | = | $C^{10}H^{12}O^{2}.C^{6}H^{4}O^{8}$ |
| Amylic Valerate | $C^{20}H^{20}O^{4}$ | = | $C^{10}H^{11}O.C^{10}H^{9}O^{3}$ |

SECONDARY NUCLEI.

*Oxygen-nucleus*, $C^{10}H^{9}O$.
Valerianic anhydride = $C^{10}H^{9}O.O^{2}$
*Oxygen-nucleus*, $C^{10}H^{8}O^{2}$.
Pyrotartaric acid = $C^{10}H^{8}O^{2}.O^{6}$
*Oxygen-nucleus*, $C^{10}H^{6}O^{2}$.
Pyrotartaric anhydride, $C^{10}H^{6}O^{4}.O^{2}$

*Chlorine-nucleus*, $C^{10}Cl^{3}H^{7}$.
Trichlorovalerianic acid, $C^{10}Cl^{3}H^{7}.O^{4}$
*Chlorine-nucleus*, $C^{10}Cl^{4}H^{6}$.
Tetrachlorovalerianic acid, $C^{10}Cl^{4}H^{6}.O^{4}$

*Amidogen-nucleus*, $C^{10}(NH^{2})H^{9} = C^{10}AdH^{9}$.

| | | | |
|---|---|---|---|
| Amylamine | $C^{10}NH^{13}$ | = | $C^{10}AdH^{9}.H^{2}$ |
| Diamylamine | $C^{20}NH^{23}$ | = | $C^{10}Ad(C^{10}H^{11})H^{8}.H^{2}$ |
| Methyl-ethyl-amylamine | $C^{16}NH^{19}$ | = | $C^{10}Ad(C^{2}H^{3})(C^{4}H^{5})H^{7}.H^{2}$ |
| Diethyl-amylamine | $C^{18}NH^{21}$ | = | $C^{10}Ad(C^{4}H^{5})^{2}H^{7}.H^{2}$ |
| Triamylamine | $C^{30}NH^{33}$ | = | $C^{10}Ad(C^{10}H^{11})^{2}H^{7}.H^{2}$ |
| Methyl-diethyl-amylamine | $C^{20}NH^{23}$ | = | $C^{10}Ad(C^{2}H^{3})(C^{4}H^{5})^{2}H^{6}.H^{2}$ |
| Triethyl-amylamine | $C^{22}NH^{25}$ | = | $C^{10}Ad(C^{4}H^{5})^{3}H^{6}.H^{2}$ |
| Tetramylamine | $C^{40}NH^{43}$ | = | $C^{10}Ad(C^{10}H^{11})^{3}H^{6}.H^{2}$ |
| Valeramide | $C^{10}NH^{11}O^{2}$ | = | $C^{10}AdH^{9}.O^{2}$ |
| Amylurethane | $C^{12}NH^{13}O^{4}$ | = | $C^{10}AdH^{11}.2CO^{2}$ |
| Oxamylane | $C^{14}NH^{13}O^{6}$ | = | $C^{10}AdH^{11}.C^{4}O^{6}$ |
| Sincaline | $C^{10}NH^{13}O^{2}$ | = | $C^{10}AdH^{11}.O^{2}$ |
| Xanthamylamide | $C^{12}NH^{13}S^{2}O^{2}$ | = | $C^{10}AdH^{11}.CS^{2}.CO^{2}$. |

*Amidogen-nucleus*, $C^{10}Ad^{2}H^{8}O^{6}$.
Inosic acid, $C^{10}N^{2}H^{8}O^{10} = C^{10}Ad^{2}H^{8}O^{6}.O^{4}$

*Azo-nucleus*, $C^{10}NH^{9}$.
Valeronitrile, $C^{10}NH^{9}$

*Conjugated Compounds.*

| | | | |
|---|---|---|---|
| Amylene-urea | $C^{12}N^{2}H^{14}O^{2}$ | = | $C^{10}H^{10}.C^{2}N^{2}H^{4}O^{2}$ |
| Valeryl-urea | $C^{12}N^{2}H^{12}O^{4}$ | = | $C^{10}H^{8}O^{2}.C^{2}N^{2}H^{4}O^{2}$ |
| Amyl-piperidine | $C^{20}NH^{21}$ | = | $C^{10}H^{10}.C^{10}AdH^{9}$ |

The nucleus theory has not been adopted in any other systematic work on Organic Chemistry, and it is perhaps unfortunate that Gmelin should have made it the basis of his arrangement of organic compounds; for it is entirely artificial, often bringing into close proximity compounds which have little or no natural relation to one another, and has moreover the radical defect of representing organic compounds as a class of bodies quite distinct from inorganic compounds, a distinction which recent investigations have shown to have no existence in nature. Still as an artificial system it is perhaps as convenient as any other, and enables us with facility to arrange and classify nearly all organic bodies whose composition has been well made out, as may be seen by reference to the preceding table, and further to the Tables of Contents of the several volumes of Gmelin's Handbook relating to organic chemistry (vols. vii.–xvi.). The objection sometimes urged against it that the number of carbon-atoms in a compound must be known before its place in the system can be determined, is not of much force; for no system that could be devised would enable an enquirer to find the place of any given compound in it without knowing something about its constitution. A more serious objection to the system is that many compounds cannot be arranged under it at all. Such compounds are placed in the Handbook as Appendices to the groups to which they appear to have the closest affinity. Thus, under the head of compounds containing 32 carbon-atoms, Linseed-oil and other drying oils are placed in an appendix to Linoleic acid; fish-oils as an appendix to Physetoleic acid; and the solid natural fats, as an appendix to the Cetylene series in general. This defect, however, is not peculiar to the nucleus-theory: indeed in classifying compounds according to the radicle-theory, we meet with at least an equal number of compounds which at present appear intractable: in Gerhardt's *Traité de Chimie organique*, for example, which is arranged according to that theory, about a fourth of the entire space is taken up with the description of "Corps à sérier."

**NUMBERS, LAW OF EVEN.** See CLASSIFICATION (i. 1011).

**NUSSIERITE.** An impure pyromorphite containing arsenate of lead, from Nussière, Dep. of Rhone, France.

**NUT OILS.** Hazel-nuts, the seed of *Corylus Avellana*, yield 60 per cent. of a colourless or pale yellow oil having a sweet taste, and a specific gravity of 0·9242 at 15°. It solidifies at −10° The cold-pressed oil was found by Lefort to contain 76·65—77·15 per cent. carbon, 11·46—11·73 hydrogen and 11·89—11·12 oxygen. It forms with *chlorine* a colourless compound rather thicker than the oil itself, of specific gravity 1·081 at 3·5°, and containing 21·06—20·25 per cent. chlorine. The *brominated* oil is yellowish, of the same consistence as the chlorine-compound, of specific gravity 1·280 at 2·3°, and containing from 36·35 to 36·58 per cent. bromine.

Walnut-oil from the kernel of *Juglans regia*, commonly called *nut oil*, is greenish when newly prepared, but becomes pale-yellow by keeping. Specific gravity 0·9283 at 12°, 0·9194 at 25°, and 0·871 at 94°. It is inodorous and has an agreeable taste. It thickens at −15° and solidifies to a white mass at −27·5° (Saussure). It dries more quickly than linseed-oil, and is therefore much used in painting.

It contains, according to Lefort, 70·7 per cent. carbon, 11·5 hydrogen, and 17·8 oxygen. Forms a soft soap with potash. Walnuts yield as much as 50 per cent. of this oil.

*Chlorine* converts walnut-oil into a light yellow butter of the consistence of thick honey: specific gravity 1·111 at 12°, and containing 27·12—27·25 per cent. chlorine. The *brominated* oil has the same consistence, a specific gravity of 1·409 at 17·5°, and contains 46·84—46·75 per cent. bromine. (Gerh. ii. 898.)

**NUTMEG OILS.** Nutmegs, the seed of *Myristica aromatica* (or *M. moschata*), yield by distillation with water, about 6 per cent. of a transparent, nearly colourless, mobile, volatile oil of specific gravity 0·948 (Lewis), 0·920 (Bley), having the odour of nutmeg, and an aromatic burning taste. It contains 81·1 per cent. carbon, 10·8 hydrogen, and 8·0 oxygen, and is a mixture of an oil and a camphor. It dissolves in alcohol and forms a soapy mass with alkalis.

The oil when left to stand deposits a camphor or stearoptene called myristicin, which dissolves easily in boiling water and crystallises therefrom on cooling in transparent colourless, long, very thin prisms with dihedral summits, or by rapid crystallisation in stellate groups of needles. It dissolves also in cold nitric acid and in aqueous potash, easily in alcohol and ether, and in warm oils, both fixed and volatile. Contains 62·1 per cent. carbon, 10·6 hydrogen, and 27·3 oxygen (Mulder), agreeing nearly with the formula $C^{10}H^{20}O^{3}$. It melts above 100°, and sublimes completely at a higher temperature in white very slender needles. It absorbs 11·8 per cent. hydrochloric acid gas, melting to a transparent mass, the aqueous solution of which is precipitated by nitrate of silver. (Gm. xvi. 391.)

The volatile oil obtained from mace or the arillus of nutmeg and the fixed oil or butter called myristin, expressed from the seeds, have been already described (iii. 740 and 1073).

**NUTRITION, ANIMAL.** The word "nutrition" as applied to animals is employed by physiologists in two somewhat different senses. They often use it in speaking of the morphological laws according to which the parts of an animal decrease or increase relatively to the whole mass of the animal and thereby bring about changes in form. It is more commonly used (and only so here) to denote, irrespective of form, the sum total of the processes through which the animal body is built up and sustained, both as to its material and as to its forces, by that fraction of the external world which it takes into itself from time to time under the name of "food." Every animal continually sets free from itself during its lifetime a certain amount of material and a certain amount of force; and the laws of nutrition mean the laws according to which that loss is continually replenished from the first moment of the animal's existence to its final dissolution. The necessity of such a continual waste and renewal, though a problem of great obscurity, so long as the older theories of vital action were believed in, becomes clear when the facts are studied in the light of the theory of the conservation of forces. While the waste of material in any vital action was supposed to be caused *by* the vital act—while, for instance, the waste of muscular substance in muscular contraction, was supposed to be caused by the play in the muscular fibre of some immaterial thing called vital force—it was difficult to connect stringently together the work and waste as cause and effect, and to show why the action of the immaterial principle should necessitate the destruction of the material substance. The difficulty however vanishes as soon as we lay aside the idea of any particular vital force or forces, and regard the force exerted by an animal upon the world outside it, as having been previously stored up within the tissues of the body as latent energy, and as being set free in various forms of actual energy by their decomposition. From this point of view, the force becomes the result, not the cause, of the waste; and a renewal of the body is necessary, not in order that the vital force may have new material through which to play, but because fresh latent energy embodied in new material is from time to time wanted for the production of actual force. An animal may thus be considered as consisting, at any epoch, of a certain amount of force associated as latent energy with a certain amount of material. During life the force is being separated from the material and set free, manifested, expended in the various forms of vital force, and the material thus deprived of its force, is being cast out as useless. This necessitates that there should be continually passing into the body a certain amount of force and a certain amount of material, so associated together that they are capable either of being divorced at once within the economy, and the actual energy liberated, as one or more of the so-called vital forces, or of becoming part and parcel of the stock of force and material represented by the body, ready when occasion demands to be similarly disposed of. Thus there are three things to be considered: the total income or material *plus* force; the force expended or work done, that is to say the sum of the vital actions of the economy; and the waste or material *minus* the expended force. The condition of the organism at any given time will depend on the relation which these factors then bear to each other. Thus in early life, the income exceeds the expenditure of force and therefore also the waste of material; consequently the organism gains both in force and material. After a certain age, however, the income within a given period is, neglecting temporary variations, sufficient, but only sufficient, to cover the expenditure: consequently the body neither gains nor loses either in force or material, but remains in a condition of equilibrium. The season then follows in which the real income is less than the expenditure, and the body becomes a loser. We might theoretically imagine this loss to continue until the organism had dwindled down to its primeval nothingness; but in reality, a more or less violent disruption of the vital machinery, called death, takes place before any great diminution can occur. The dead body then represents a certain amount of force and material ready to be disjoined and dissipated in ways that are not vital through the so-called putrefactive decomposition. These relations of the factors to each other during the several phases of a lifetime are imitated in the temporary variations that occur from day to day or year to year.

In considering the *income* or *ingesta*, we find that, although an animal receives small quantities of actual energy in the shape of heat, electricity, motion, &c., these are so insignificant that they may be disregarded when compared with the other sources of force. Every animal takes into itself from time to time a certain amount of a certain number of substances, including a certain quantity of oxygen. These substances represent, in the prospect of their chemical union, a certain amount of latent energy (*Spannkraft*); it is their latent energy which forms almost entirely the source of the actual energy of the organism. Since the particular chemical union through which the latent energy of these substances becomes liberated as actual energy, is chiefly one of oxidation, we are enabled to state that the income of force for animals is the force derived from the oxidation by the oxygen of respiration of the oxidisable bodies taken as food.

The force expended, or *effectus*, of the animal assumes various forms. A certain portion becomes, and issues as, heat. Another quantity is represented by muscular contraction, part of which is concerned in visceral movements, while the rest results in locomotion and other mechanical effects. A third quantity is called nervous, or cerebral, or sometimes mental force. A fourth is occupied with growth and the preservation of form. The remainder has to do with the chemical transformations and elaborations which are necessary before the brute food is in a proper state to be consumed in vital action. A part of the total income is expended in raising the rest of the ingested material, with its latent energy, to a higher level of concentration and adaptability for conversion, in changing, as it is said, the dead meat and vegetable substance into living flesh and blood through the processes of digestion, assimilation, &c. This may be called, par excellence, nutritive work; it corresponds also to the force supposed by some writers to be required by living material in order to resist ordinary chemical and physical changes.

The *waste* or *egesta* may be briefly described as consisting of carbonic acid, water and certain crystalline nitrogenous bodies, of which urea is the physiological type, together with a few other matters always associated with the latter. All these are the results of the oxidation of the oxidisable income.

It is evident that the task of taking the force and material of the income and of explaining the numerous conversions they suffer until they finally issue as effectus and egesta, is nothing else than the whole task of physiology. The study of nutrition must of necessity be confined within narrower limits, perhaps in some such way as follows. The animal body consists of certain kinds of material with force so associated with them, that the decomposition, the metamorphosis, in other words the oxidation, of each material sets free an appropriate force and gives rise to a corresponding waste. Thus among other things, the body contains certain quantities of nervous, muscular and adipose tissue, whose decomposition may be said to give rise to muscular, nervous, and calorific action, the development of each action being accompanied by its particular waste. The object of the study of nutrition is to ascertain qualitatively and quantitatively the things which are best suited when taken into the body to ensure the acquirement of one, several, or all of the various corporeal constituents, and thence to guarantee the exhibition of the force or forces proper to the animal; or, in other words, to determine the laws according to which qualitative and quantitative variations of the income affect the quality and quantity of the capital, and thence the quality and quantity of the expenditure. The practical problems, for whose solutions a knowledge of such laws is desirable, will vary of course with the circumstances of the animal. For instance in animals doomed to the slaughter-house, the questions have to deal more particularly with the amount and nature of the material developed in the body, that is to say with the amount and character of the capital. In man and beasts of burden, attention has to be drawn to the amount and nature of the force expended, muscular, nervous, &c. In coming to any conclusion on these matters, a certain amount of crude experience is necessary before a rigorously scientific method can be applied.

## On the Nature of Food,

that is to say, the nature of the income. Though oxygen is an essential part of the income, it stands so much apart by itself, that it is generally considered separately from the rest of the income or food proper. Experience teaches us that the food of animals, so understood, consists of a certain number of animal, vegetable, and inorganic substances known under the name of "articles of food." Such are meat, bread, milk, potatoes, grass, water. Some animals (*herbivora*) feed on vegetable and inorganic substances only, viz. plants and water. Others (*carnivora*) feed only on animals (previously reared on vegetables) and water. Others again, such as man, are omnivorous, feeding on both animals and plants. A chemical examination of all known "articles of food" shows that each of them contains one member or several members of a class of chemical compounds, which, from their universal occurrence in the exceedingly numerous and otherwise most diversely constituted "articles of food," and from the constant ratio their presence bears to the roughly determined nutritive value of these articles, have received the name of "alimentary principles." They have these characteristics. They are all capable of being digested, *i.e.* of passing from the alimentary canal into the system; when any one of them is swallowed, a fraction only of it reappears in the fæces. They are all capable of being oxidised, and are found by observation to be more or less completely oxidised when introduced into the system as food; when swallowed, the part which does not reappear in the fæces, and which therefore has been digested and absorbed, cannot be detected passing outwards again unaltered, either through kidneys, lungs or skin. They are nearly all complex compounds of carbon, hydrogen, oxygen and nitrogen.

Besides these oxidisable "alimentary principles" there is also another class of substances, represented by some of its members in every article of food, substances which, though digestible and evidently in the habit of passing into the system, are either incapable of oxidation or may be proved not to be oxidised in their transit through the economy. In the opinion of some, these bodies should not be classed under the head of food. But there are cogent reasons why they should be so treated. Experience shows that they are quite as essential constituents of a healthy diet as their oxidisable companions. And the necessity for their use is obvious. If it is true that the amount of force possessed and given out by living beings, is due to the chemical processes taking place within the body, or speaking generally, to the oxidation of the oxidisable food; then, out of the whole number of substances consumed as food, only the oxidisable "alimentary principles" can be looked to as sources of force. But life is not mere naked force; it is not simple combustion or oxidation. It is oxidation under particular circumstances; it is force manifested in particular modes. The force generated by the oxidation of the alimentary principles is regulated and directed into particular channels in and by the body. The body itself, besides being a mass of latent force, is a machine for the conversion of force, and that part of the body which so serves as mere machinery will require for its construction, material that not only need not be oxidisable and force-giving, but will be all the more useful for its special purposes in so far as it cannot be oxidised. While that machinery is being built up, during the growth of the animal, its material must be sought for in food, and during the whole of the life-time there will be continual waste and renewal of the machinery, not necessarily for the purpose of giving forth force, but because the peculiar circumstances of the machinery unavoidably cause part of it to be continually carried off in the general waste-current of the economy. The animal body is not a steam-engine which seeks only force in its fuel and is repaired from without; it is a peculiar machine which has to find in its food not only its supply of force but also material for its constant repair. We may therefore divide food into the oxidisable alimentary principles, the force-generators, the biogenic elements, and into the other substances which serve only as material for repair of pure machinery, and which therefore may be called force-regulators or biotaxic elements. It must however be remembered that the force-generators may be or rather decidedly are force-regulators, though the converse of course does not hold good. It is naturally a matter of very great difficulty to determine whether any given body, confessedly not an alimentary principle, is to be regarded as a force-regulator, or as being in that sense necessary to the well-being of the economy.

All such substances, generally found in a healthy body and therefore in ordinary food and in the ordinary egesta, may be so considered. But it would be hazardous to limit the list to these, since it is quite possible that science may yet discover that the ordinary consumption of bodies not as yet recommended by experience would increase an animal's well-being by introducing "new regulative elements" whereby the conversions of force within the economy might be more advantageously carried on. Should any such be discovered, they would have the right to be claimed as proper elements of food. Hence the difficulty of giving a satisfactory definition of "food" wide enough to embrace all its parts. "Whatever is commonly insorbed in a state of health" is perhaps the best or rather the truest. According to this quinine (which though oxidised in the system to a certain extent, must be regarded for its virtues as a pure regulator) in the midst of malaria is as much an element of food as starch or salt. Medicines in general may be regarded as occasional regulators.

The alimentary principles may be roughly enumerated as follows:

1. *Nitrogenous Colloïds.*—These are chiefly the whole series of protein-compounds or albuminoïds, both from the animal and vegetable kingdoms. Also gelatin, which though of little value apparently for certain purposes, fairly comes under the head of "alimentary principles." To these may be added certain peculiar nitrogenous compounds, not protein, such as those occurring in beet-root molasses or mangold pulp (Henneberg and Stohmann) whose nature and properties have not yet been well studied.

2. *Hydrocarbons, Fats.*—Nearly all animal fats may be regarded as alimentary principles. So also most of the vegetable fatty bodies, with deductions for varying digestibility and purity. Information as to the digestibility of vegetable bodies more or less allied to fats and oils is wanting. According to Grouven, the waxy and resinous portions of vegetable food are largely digested by oxen and oxidised in their system.

3. *Carbo-hydrates.*—Starch, Sugars, Dextrin, Gum, Woody-fibre, Pectin. The first two are largely present in most vegetable articles of food, and hold a high rank as alimentary principles. Inulin, according to Rolleston (Brit. Assoc. Reports, 1862), resists human salivary diastase, and is possibly therefore not digested. Gum is not digested by man, but is destroyed in considerable quantities by oxen (Grouven). The group of substances known under the name of pectin, classed for convenience with carbohydrates, seems to be readily digested and oxidised by oxen. Woody-fibre (that is the cellulose of woody-fibre, not its lignin or cutin) is digested by ruminants to the extent of from 30—60 per cent. (Lawes and Gilbert, Henneberg, Grouven.)

Besides these alimentary principles there are also present in a healthy diet, the bodies which have been called regulators, viz.:

Water, and the following elements in various combinations, phosphorus, sulphur (in addition to the quantities contained in the protein substances), chlorine, fluorine, sodium, potassium, calcium, magnesium, iron, silicon.

There are also consumed in food, either universally, or generally, or occasionally, certain bodies most of them capable of oxidation, but concerning which there is much dispute, either as to whether they really are oxidised in the system, or as to whether, if oxidised, their value as ingredients of food is to be measured by the force given out by their oxidation, or by their action as regulators. Such are vegetable acids, theine, alcohol, &c.

The food of man also contains certain substances known under the name of condiments. Since these bodies perform their functions outside the real body though within the alimentary canal, they have no better reason to be considered as food than has hunger, *optimum condimentum.*

### DIETETICS.

Crude experience teaches how to form such a mixture of these elements of food as shall ensure the well-being of the animal, in other words how to construct a healthy diet. It is found that when any one alimentary principle is alone taken as food, the animal perishes by starvation. Neither protein, nor fat, nor starch, nor sugar can alone support life. It is also found that animals cannot be maintained in health unless some members of the group of elements called regulators are present in their food. Hence the rule may be laid down that every good diet must consist of two or more alimentary principles combined with a selection of regulators. Every known article of food fulfils these conditions more or less perfectly. In order to obtain from experience more exact knowledge of the absolute and relative amounts of the constituents of a healthy diet, recourse must be had to statistical analysis. Thus, taking man as an example, if a large number of diets actually in use among persons of average circumstances be collected, and the various articles of food contained in each be analysed according to their alimentary principles and constituents, a mean may be drawn which would give a qualitative and quantitative selection of the chief factors for a normal diet. Thus Moleschott (Phys. d. Nahrungsmittel. s. 216) gives as a normal daily diet, protein-substance, 130 grms.; fat, 84 grms.; starch, 404 grms.; salt, 30 grms.; water, 2,800 grms. Since no one article of food contains its alimentary constituents in that proportion, it is evident that two or more articles of food are necessary for a good diet. Another method of formulating the results of large experience, is to express them, not in terms of the alimentary principles themselves, but in terms of the total quantity of nitrogen and carbon contained in those principles. Thus a certain amount of nitrogen represents a certain amount of protein, and a certain amount of carbon also represents the same amount of protein, plus a certain quantity of either fat, starch, or sugar, &c., or of all of them. In this way Dr. Edward Smith (Sixth Report Med. Off. Privy Council) calculates that the agricultural poor of Great Britain consume on an average 420 grms. carbon, and 20 grms. nitrogen daily, while silk-weavers, needlewomen, &c., only get 267 grms. carbon, and 11 grms. nitrogen. Since the latter only just manage to keep starvation from their doors (265 grms. carbon, and 12 grms. nitrogen daily being the "starvation diet" suggested by Dr. Smith in reference to the Lancashire operatives), the diet of the former, productive as it appears to be of general health, may fairly be taken as a normal diet. Variations, however, from such a standard, often extreme in character and yet compatible with well-being, are occasionally witnessed. Thus Carpenter (Human Phys. p. 46) remarks on the voracity of the Esquimaux, and quotes an instance of one devouring 35 lbs. of aliment mostly fatty. Such a meal was probably rather swallowed than digested; but the case of the voyageurs of Canada, who are dissatisfied with rations short of 20 lbs. of meat per diem, would give a consumption of 280 grms. nitrogen. In the direction of a minimum the same author mentions an instance of a miller, who lived in vigour for 18 years on 16 oz. of flour per diem, which would give 110 grms. carbon, and 5·8 grms. nitrogen. Since this miller drank no alcohol, his case somewhat lessens the value of an argument founded on the histories of individuals said to have lived for years on spirits plus a small quantity of actual food.

Another method of determining a normal diet consists in estimating the average quantity of nitrogen and carbon in the urea and carbonic acid of the egesta. The amount thus determined is first translated into alimentary principles, and thence into articles of food. The lessons of experience thus roughly analysed, though of course very valuable, cannot be regarded as anything more than approximations to truth, or as bases for further inquiry. For instance they take no account of an exceedingly variable factor in the matter, namely digestibility. Thus the diet gained by calculat-

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ing back from the egesta can only be a true one when the whole of the ingesta are digested, which is probably never the case. So again in the method adopted by Dr. E. Smith, it is taken for granted that the articles of food containing the one nitrogen and carbon are either wholly digested or digested at the same rates under all circumstances. But we know that the digestibility of the different alimentary principles varies according to the nature of the article of food in which they are presented. And not only has each article of food an absolute coefficient of digestibility, but there is every reason to believe that in a mixture of different kinds of food such as forms an ordinary meal, the amount digested of each constituent will vary according to the proportions and character of the mixture. Thus the presence of fat is thought to assist the digestion of starch, and the amount of cellulose digested by oxen varies according to the amount of other substances present in the rations (Henneberg, Gronven). Other circumstances too, such as labour, rest, &c., materially affect digestion (E. Smith). Hence the importance of estimating, not the amount of food taken in by the mouth only, but that which is really absorbed into the system and which alone possesses the virtues sought for. Even when the actual amount of carbon and nitrogen necessary for use under average circumstances has been thus determined, several questions have to be answered before a diet of any practical use can be fixed upon. Can gelatin supplant protein either wholly or in part? The labours of the well-known commissions show how difficult or rather impossible it is to decide this from mere experience. Are fat and starch mutually convertible? May a diet consist of all fat or all starch in addition to the protein? Is the action of sugar the same as that of starch? What changes should be made for labour? What for fattening? It is evident that to determine questions like these from mere experience, with nothing but the vague condition of well-being as a test of success, is well-nigh impossible. For further knowledge it becomes necessary to leave on one side the concrete results of experience either with regard to man or animals, and to turn to the search of the abstract laws governing the conversion (in the animal body) of ingesta into effectus and egesta.

## General Laws of Nutrition,

Or, the laws according to which material consumed as food affects the composition, and forces of the animal organism.

The older views on this matter were extremely simple. Dumas (*Essai de Statique Chimique des Êtres organisés*) taught that all the alimentary principles might be divided into, 1. *Assimilable products*, viz. protein substances and fatty bodies which served by direct assimilation, to increase or renew the organs of the body previously wasted during the exercise of vital forces; and 2. *Combustible products*, viz. sugar and fatty bodies, consumed in respiration for the purpose of supplying animal heat. Liebig and his school proved that fat was actually created in the animal economy probably out of the carbo-hydrates (Dumas having at first said, "L'animal s'assimile donc ou détruit des matières organiques toutes faites; il n'en crée donc pas," but afterwards supporting Liebig's view); and hence, while adopting a similar division of food into "plastic" and "respiratory" elements, added as a corollary that an excess of ingested respiratory material not wanted for immediate use, might be stored up in the body, not as fully formed tissue, but as mechanically infiltrated fat. Since then, however, the matter has been the subject of much exact inquiry; and the results obtained will be best studied by considering the statics, that is, all that relates to composition, apart from the dynamics which have to do with force.

### A. *Statics.*

The following is the general form of the problems to be dealt with. Given the effect of a known ration of food on the total weight of an animal, to determine, from an elementary comparison between the ingesta and egesta, how that effect may be described in terms of the constituents of the body. For this purpose, an analysis, proximate and elementary, of the food consumed within a given time is made; the urine and fæces are collected and analysed, their elementary composition being directly determined if perfect exactitude is required; the excretion by lungs and skin is also estimated by means of a "respiration-chamber," and the amount of oxygen fixed by respiration calculated by subtracting the initial weight of the animal plus its food from the final weight plus all the egesta. With what great certainty such a comparison may be made is seen from the following table of the observations made by Pettenkofer and Voit on a dog, who with a daily ration of 1,500 grms. of meat was neither materially gaining nor losing flesh.

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Ingesta = 1500 grms. Meat.

| | | | |
|---|---|---|---|
| 187·8 | grms. | Carbon. | |
| 152·45 | „ | Hydrogen | 25·95 in dry-substance.<br>126·5 in water. |
| 51·00 | „ | Nitrogen | |
| 1089·25 | „ | Oxygen | 77·25 in dry-substance.<br>1012· in water. |
| 19·5 | „ | Salts | |

*Oxygen* fixed = 477·2.

Egesta in grms.

| | Carbon. | Hydrogen. | Nitrogen. | Oxygen. | Salts. |
|---|---|---|---|---|---|
| Urea | 21·6 | 7·2 | 50·4 | 28·8 | |
| Other urinary constituents | 9·6 | 2·5 | . . | 15·9 | 16·3 |
| Water of urine | . . | 102·5 | . . | 820·3 | |
| Dry Fæces | 4·9 | 0·7 | 0·7 | 1·5 | 3·4 |
| Water of Fæces | . . | 3·2 | . . | 26·3 | |
| Carbonic Acid of Perspiration* | 146·7 | | . . | 391·5 | |
| Marsh Gas of Perspiration | 1·2 | 0·4 | | | |
| Free Hydrogen of Perspiration | . . | 1·4 | | | |
| Water of Perspiration | . . | 39·4 | . . | 315·4 | |
| *Total Egesta* | 184·0 | 157·3 | 51·1 | 1599·7 | 19·7 |
| *Total Ingesta* | 187·8 | 152·5 | 51· | 1566·4 | 19·5 |

Sum of Ingesta . . 1977·2 }
„ „ Egesta . . 2011·8 } Difference = 34·6.

And even this slight difference the observers state might be still further reduced by hypothetical corrections, for fæces, of the animal's total weight. In all experiments of this kind, the determination of the real weight of the animal, though apparently easy, is in reality a very difficult task, inasmuch as the total body-weight forming the basis of the calculations ought to be that of the body free from fæces, and in most cases the animal has within him at the time of the initial weighing some of the fæces of his previous diet, and at the final weighing more or less of the fæces formed out of his experimental rations. In the observation above detailed the carbonic acid, water of perspiration, &c., &c., were directly determined by means of a complicated apparatus. Other inquirers have been content to determine the carbonic acid only, and that from time to time during the experiment (Bidder and Schmidt), leaving the water of perspiration for calculation, and neglecting the other gaseous excreta altogether. Bischof and Voit did not even determine the carbonic acid, but based their calculations on the average thrown off by dogs according to Regnault and Reiset.

The determination of the nitrogen of the egesta has been the occasion of much dispute. In the above observation, Pettenkofer and Voit merely determined by Liebig's method the urea of the urine, and considered the nitrogen therein contained as the only nitrogen excreted. Against this mode of procedure, it has been urged, in the first place, that the urine certainly does contain small quantities of other nitrogenous bodies, to wit, creatine, creatinine, &c., and may possibly contain them in considerable quantities on particular occasions. Voit maintains however that Liebig's method gives a result which includes these bodies when they are present, "their nitrogen-equivalent behaving towards the mercurial solution exactly like the nitrogen-equivalent of urea." Other observers have determined the uric acid as well (Ranke), or in herbivora the hippuric acid (Henneberg, Gronven). It is also urged that a certain quantity, a small one doubtless, of nitrogen goes off in the process of desquamation and depilation. This has been approximatively accounted for by some observers (Bidder and Schmidt, Gronven). Lastly, it is maintained that nitrogen passes off by skin and lungs in some form or another in considerable quantity. While Regnault and Reiset found evidence of only slight exhalation or absorption of nitrogen by the lungs, Boussingault (Mem. de Chimie agricole, &c.), in experimenting on turtle-doves and horses, could only recover from urine and fæces about two-thirds of the total quantity of nitrogen taken in as food. Barral, experimenting on human beings, came to a similar conclusion; and other observers have failed to a greater or less extent in recovering from urine and fæces the nitrogen of the aliment. More recently Reiset (Ann. Ch. Phys. 1863) found evidence of considerable volatile excretion of nitrogen in sheep, calves, geese and turkey-fowls, and to a small extent in pigs. To these facts may be added the experiments of Fnnke on the presence in the perspiration, of urea in considerable quantities. On the other hand, Bidder and Schmidt found in cats the whole of the nitrogen reappearing in urine and fæces, except in cases where there was reason to think it had been retained in the body. Haughton (Dublin Quart. Med. J. 1859) believes that the same thing holds good with men, and that Barral was wrong in his analysis of food. So also Ranke, who moreover found both that a profuse sweat had no effect on the nitrogen of urine, and that there was no appreciable amount of nitrogen to be discovered in the sweat. Henneberg holds apparently that in oxen no decided amount of nitrogen is lost by lungs or skin (except as hairs, &c.), and Gronven found by direct estimation, the amount of ammonia given off by oxen to be exceedingly small (¼ grm. per diem); he also ascertained that the difference between the nitrogen of food and that of urine and fæces was reduced to a very small quantity indeed when the ox was fed for some considerable time on rations whereby he neither gained nor lost much in flesh. Lastly, Voit (Ann. Ch. Pharm. Suppl. ii. 1863) fed a pigeon in the same manner as Boussingault for a considerable time on fixed rations, and found that he could recover out of urine and fæces all the nitrogen of the food with the exception of 2·3 per cent., which moreover could be accounted for by considering an increase which took place in the animal's weight to be an increase in nitrogenous material. Voit calculated that if only 0·11 grm. nitrogen had been given out daily by the skin and lungs, in addition to that contained in urine and fæces, there would have been none left in the animal's body at the end of the experiment! Hence in experiments of this kind the practice still obtains of considering the nitrogen of the urea (with that of uric and hippuric acids when present) as representing the whole nitrogen of the egesta.

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* By skin and lungs.

Having thus determined with more or less precision the amount and nature of the egesta, the fæces must be placed in a division by themselves, since they represent the portion of food which is not digested, not absorbed within the true body, which takes no share in the actions of the economy, and must therefore be deducted from the total of food, the effect of which is being studied. It is quite true that the fæces contain, besides undigested material, a certain amount of stuff which has been poured into the intestine after having fulfilled its function in the economy, and has escaped resorption during its transit through the alimentary canal; but the amount which has thus undergone oxidation is so small that it is generally disregarded.

The next thing to be done is to determine what inference is to be drawn from the presence in the true egesta (from kidney, skin and lungs) of any given element or compound. What, for instance, does the presence of nitrogen (or urea) signify? The nitrogen arises doubtless from some metamorphosis within the body (metamorphosis being used as meaning chemical change, a shifting of the elements from one formula into another, or others). We may go so far as to say that it arises from the metamorphosis of some nitrogenous material, which material may further be declared to be a protein substance (or gelatin).

But there are in the animal organism many different proteinous tissues, and at least more than one gelatiniferous substance (holding positions of variable importance and value), each of which might by metamorphosis give rise to the nitrogen of the egesta. If we take the very roughest analysis of the animal body, we shall be obliged to consider, as separate collections of nitrogenous material, the muscular tissue, the nervous tissue, the connective tissue (including the bones), the glandular tissue, and blood, each containing not only a form and possibly several forms of nitrogenous material, but very many other substances as well. And it is evident that if we assume that the presence of a given quantity of nitrogen in the urine indicates the metamorphosis of a certain quantity of any particular tissue (that metamorphosis not being confined to its nitrogenous material alone, but embracing also at least all its constituents that are at all liable to decomposition), the total change both as to the composition and the forces of the body which we are thereby enabled to predicate, will vary considerably according to the tissue which we select, whether muscular, nervous, &c., &c. Such a selection is naturally a problem of extreme difficulty; indeed it has hardly yet been attempted except in reference to two points. In the first place there is every reason to believe that the amount of metamorphosis naturally occurring in connective tissue is exceedingly small compared with that going on in the other nitrogenous tissues. Exact information on this score is wanting, but the starvation experiments have shown that the bones for instance suffer scarcely any loss during a long abstinence from food. Hence in the researches we are dealing with, the gelatiniferous tissues are disregarded. In the next place, a distinction has been set up between nitrogenous material which has merely been digested and absorbed into the blood, and nitrogenous material which has undergone the further process of being converted or assimilated into actual tissue with distinct anatomical elements. For instance, a certain quantity of albumin having been converted by the stomach into the peptones, enters the circulation and forms part of the nitrogenous material of the blood; in due time it escapes from the capillaries and comes into close connection with some tissue, say muscular fibre, of which it is henceforth a component part (though how far each chemical constituent of a muscle has to do with its histological features, the nuclei, striæ, &c., or how far these same features share in the general metamorphosis of the fibre is uncertain). If the albumin is metamorphosed so as to give rise to urea while it is still within the blood, the result to the organism will be very different from what would occur if the metamorphosis were deferred until the albumin had become part and parcel of the muscular fibre. And the same applies to the other tissues. Hence we may speak broadly of two sources of urea; one, the metamorphosis of digested food still dwelling in the blood-current, and which, for the sake of brevity, we may call the metamorphosis of *Blastema* or modified food; the other, the metamorphosis of tissue previously formed out of Blood, and which we may call *Flesh*, although we embrace under that title not muscular tissue only, but every other kind of tissue that contains nitrogenous material subject to constant change. According to **Liebig**, **Bischof**, **Voit** and others, the last only is the true expression of the process of the economy, Flesh the only source of urea. According to **Bidder** and **Schmidt** urea may arise both from Blastema and from Flesh.

Having thus determined the source of the nitrogen, the analysis of the egesta may be continued. The metamorphosis of Flesh or Blastema (or both) which accounts for the nitrogen will also account for a certain quantity of carbon, hydrogen and oxygen. The remaining quantity may then be inferred to result either from the metamorphosis of a calculable quantity of adipose tissue (or Fat) or from the metamorphosis of the hydrocarbons or carbo-hydrates of Food while still in the blood-current (Blastema). A comparison of the ingesta and egesta may then be used as follows.

An excess of the nitrogen in the ingesta over that in the egesta will be regarded as a storing up of nitrogenous material which has escaped metamorphosis—as a gain either of Flesh or, if it is possible to heap up such matters in the blood-current, of Blastema. An excess of nitrogen in the egesta over that in the ingesta will signify a metamorphosis or consumption of Flesh over and above the metamorphosis of nitrogenous material contained in the food (or its equivalent in flesh), and therefore may be regarded as a loss of flesh. Supposing there to have been during the period of experimentation a total gain $= t$, and a gain of Flesh $= a$; $t - a$ will then remain as the expression of the gain in fat, water, or both $= b + c$. The excess of carbon in the egesta over that in the ingesta minus the elements required for the gain in Flesh, may then be used for calculating the gain in Fat $= b$. The retained water may then be calculated from the equation $t - a - b = c$, and ought also to be represented (if a complete analysis of both ingesta and egesta has been made) by the amount of oxygen and hydrogen remaining in the excess of egesta after the subtraction of the elements required for the gain of Flesh and Fat. When there is a total loss, or special loss of any of these three chief constituents, the sign in the equations must be altered accordingly. As was stated above, **Bischof** and **Voit** made no complete analysis of the egesta, but contented themselves with determining the nitrogen as urea and calculating out the carbon of the egesta, as an index for gain or loss in fat, from previously determined averages of the carbonic acid exhaled and units of heat thrown off by the dog. It is evident that such calculations leave margins for very considerable errors, and a comparison between the theoretical results of Bischof and Voit, and the actually observed results of Pettenkofer and Voit *with the same dog* shows how important such errors may be.

The opinion that the nitrogen of the egesta when food is taken arises from the metamorphosis of both flesh and blood is upheld by **Bidder** and **Schmidt**. These observers determined the excreta in a cat for a period of eighteen days, during which no food at all was taken, and the whole nitrogenous metamorphosis referred therefore to flesh alone. The following table gives, reduced for each 24 hours to 1 kilogrm. of the weight on that day, the excretion of urea and carbonic acid, and also the amount of fat and dry nitrogenous protein material (not flesh) calculated to have undergone metamorphosis:

| Day. | Urea. | Carbonic acid. | Protein. | Fat. | Day. | Urea. | Carbonic acid. | Protein. | Fat. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3·437 | 20·68 | 9·94 | 1·76 | 10 | 1·907 | 22·46 | 5·78 | 4·66 |
| 2 | 2·298 | 20·61 | 7·13 | 3·30 | 11 | 1·723 | 22·09 | 5·34 | 4·84 |
| 3 | 1·887 | 21·57 | 5·85 | 4·34 | 12 | 1·648 | 23·13 | 5·12 | 5·34 |
| 4 | 1·732 | 20·74 | 5·37 | 4·33 | 13 | 2·166 | 23·61 | 6·71 | 4·56 |
| 5 | 2·227 | 20·51 | 6·90 | 3·41 | 14 | 2 224 | 23·55 | 6·90 | 4·43 |
| 6 | 2·133 | 20·94 | 6·61 | 3·67 | 15 | 2·052 | 23·96 | 6·36 | 4·87 |
| 7 | 1·968 | 20·69 | 6·10 | 3·86 | 16 | 2·154 | 23·28 | 6·68 | 4·44 |
| 8 | 2·091 | 20·79 | 6·51 | 3·72 | 17 | 1·216 | 21·45 | 3·77 | 5·42 |
| 9 | 2·263 | 21·89 | 7·02 | 3·89 | 18 | 0·597 | 17·57 | 1·85 | 5·15 |

It will be observed that if the two first and two last days be omitted (and the influence of previous food on the one hand and of dying on the other be thus eliminated) the amount of urea and of carbonic acid excreted, and of protein and fat metamorphosed per kilogramme per diem is remarkably constant. The total quantity of nitrogen excreted during the whole period, 30·807 grms. bespoke 204·43 grms. protein material (calculated as dry muscle free from fat), containing 102·24 grms. carbon, which deducted from the total amount of carbon excreted, viz. 205·96 grms., gave 103·72 grms. carbon, an equivalent for 132·75 grms. pure fat (not adipose tissue). The total loss in weight was 1264·8 grms., which leaves 927·62 grms. for the loss in water and salts. An analysis of the dead body, compared with an analysis of another cat very closely resembling what the dead one was at the commencement of the experiment, gave a probable loss of 1020 grms. water, and 306 grms. dry material of which about 130 grms. was fat, and thus afforded a fair corroboration of the theoretical deductions. On feeding a cat, however, on such a quantity of flesh that for nine days it neither gained nor lost weight to any great extent, they found the daily excretion per kilogramme per diem to be

Urea . . . . . 2·958 Carbonic acid . . . . 20·322;

when it was forced to eat as much as possible, the excretion per kilogramme per diem was

Urea . . . . . 5·152 Carbonic acid . . . . 34·877.

Another cat left to feed ad libitum gave per kilogramme per diem

Urea . . . . . 7·663 Carbonic acid . . . . 34·164.

Bidder and Schmidt drew from their results the conclusion that the total metamorphosis of any given animal is dependent on two circumstances, or is a function of two factors, one constant, the other variable. The constant is the typical metamorphosis exhibited during hunger, shown so clearly for the cat in their starvation-experiment, a metamorphosis rendered necessary for the production of heat and the other vital forces, the amount being determined by the species, age, bulk, &c., of the animal. The variable is the food taken for the time being. When the food taken is only sufficient to cover the waste caused by the typical constant metamorphosis, all the excreta may be inferred to have arisen from the metamorphosis of flesh. When, however, a surplus of food is taken, then part of the excreta is due to metamorphosis of blastema. Thus when a surplus of meat was consumed by the cat, a certain portion entered in a state of flesh, replacing a certain quantity whose nitrogen appeared in the egesta under the form of urea as the representative of the "constant" metamorphosis; the rest was split up in the blood into a nitrogenous and hydrocarbonous portion. The nitrogenous portion was at once thrown off as urea. A certain amount of the hydrocarbonous portion then either entered the body as fat in order to supply the waste caused by the "constant metamorphosis" necessary to produce the typical amount of carbonic acid, or what amounts to the same thing, was metamorphosed at once in the blood in order to produce that amount of carbonic acid, and so saved the fat of the body from consumption. If, after the performance of this duty, any of the hydrocarbonous portion still remained, it too was metamorphosed or oxidised within the blood, limitation being made for the quantity of oxygen present. The quantity of nitrogenous material thus metamorphosed directly in the blood and thrown off as urea, was designated by Bidder and Schmidt the "Luxus-consumption." It is naturally very high with a diet of pure flesh, a large amount of albumin requiring to be split up in order to supply the necessary quantity of carbonic acid. It is reduced by the addition of hydrocarbons or carbohydrates to the food, and hence is more marked in carnivora than in herbivora.

This view of Bidder and Schmidt's is moreover supported by the fact, agreed to by nearly all observers, that the amount of urea in the urine increases very considerably within a few hours after taking food. It is thought highly improbable that in so short a space of time the food should have actually been transformed into tissue. According to Dr. E. Smith, however, this post-cibum rise of urea is not so marked as other observers have taught, especially when the hourly variations in the quantity of urea which occur during hunger are taken into consideration. Besides which it must be remembered that we do not at all know either how rapid the changes in living flesh may be, or, as was observed above, how far the anatomical elements, the formed solid portions of the tissues, for in them lies the difficulty, take part in those changes.

Another argument for the luxus-consumption is drawn from the experiments of Dr. Hammond, who found, with a purely albuminous diet, great increase of urea with great loss of strength. But to this it may be answered that the exact relation between nitrogenous metamorphosis and the production of vital force is not yet fully established; that it is quite possible that excessive metamorphosis of even muscular tissue should take place, and yet the force so liberated not take on the form of muscular power; and moreover, that urea need not necessarily be assumed to arise from muscular tissue alone, but might be supplied from all the formed tissues which we have classed together under the head of flesh. The phenomena of the disease called Diabetes, again, offer several important lessons on this point. Thus Ringer (Med. Chir. Trans. xliii.) having observed in that malady, during hunger as well as after a non-amylaceous meal,

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a constant ratio between the amount of sugar and of urea present in the urine, naturally infers the existence of a common source for both; and finding reasons for believing that the sugar, at least in some forms of diabetes, comes, not from the tissues generally, but from the liver in particular, argues that the urea comes from the same organ too, both perhaps arising from a splitting up of protein substance. **Haughton** also supports the same view. But the theory of a luxus-consumption requires that the urea should not come from a metamorphosis of the liver, but of the blood, or rather of the blastema, as it passes through the liver. And these two things have not been held sufficiently distinct. The basis of Bidder and Schmidt's views was the constant ratio of urea to body-weight which was maintained during the whole of the starvation-experiment. The truthfulness of the result has, however, been impugned by the observations of **Bischof** and **Voit**. They submitted a dog to a hunger-experiment on five different occasions:—1. After a very rich meat diet.—2. After a meat-diet decreasing gradually in amount, the last day's diet being 178 grms. meat.—3. After a very rich diet of 1,800 grms. meat and 250 grms. fat daily for 7 days.—4. After several days of a diet of 176 grms. meat and from 50–250 fat daily.—5. After being fed for several days with meat decreasing from 700 grms. to 150 grms. daily, and variable quantity of fat, and for the last two days on about 350 grms. fat only. The following table shows the amount of urea excreted per kilogramme per diem, for each day. The duration of each experiment varied considerably.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. |
|---|---|---|---|---|---|
| First day . . . | ·72 grm. | ·52 grm. | ·92 grm. | ·34 grm. | ·14 grm. |
| Second day . . . | ·77 „ | ·52 „ | ·55 „ | | |
| Third day . . . | ·70 „ | ·49 „ | ·42 „ | | |
| Fourth day . . . | ·64 „ | | ·38 „ | | |
| Fifth day . . . | ·42 „ | | ·33 „ | | |
| Sixth day . . . | ·49 „ | | ·33 „ | | |
| Seventh day . . . . | | | ·32 „ | | |

The excretion of urea per kilogramme per diem for the last two days of the diet in each case was—

| | | | | | |
|---|---|---|---|---|---|
| Last day but one . . | 3·94 grms. | ·81 grm. | 3·18 grms. | ·74 grm. | ·36 grm. |
| Last day . . . | 3·99 „ | ·78 „ | 3·22 „ | ·55 „ | ·35 „ |

From these figures it is clear that there was in the case of this dog no constant ratio of urea to body-weight at all. It is true that in none of the experiments was the period of inanition so prolonged as in Bidder and Schmidt's experiment, and therefore the possible effect of food still contained in the body not so thoroughly eliminated. But in the cat the constant ratio was reached on the second or at furthest the third day, and in the dog the amount of urea passed during the two days preceding inanition, shows that in no case could the urea of the second or even first day of hunger be supposed to have arisen to any great extent, directly from the food of the previous days. Bidder and Schmidt believed the typical amount of urea passed during starvation, bespeaking the typical amount of nitrogeneous tissue undergoing metamorphosis, to be determined by the typical amount of vital force necessary for the sustenance of life. The immense difference between ·92 and ·14 occurring in the same animal with surrounding circumstances nearly the same, and therefore most probably with the same demand for the exercise of the forces of life, shows very clearly that the amount of metamorphosis ought not be considered as depending solely on the call for the manifestation of vital energy. But if so, the idea of the typical amount of urea must be thrown on one side, and consequently the theory of the luxus-consumption deprived of its base. On the other hand, if we reflect that in series Nos. 1 and 3 the dog had lived for some time on a diet afterwards determined to be very effectual towards the storing up of nitrogenous material, in No. 2 on a diet less effectual for that purpose, in Nos. 4 and 5 on one still less so, and that therefore the amount of nitrogenous material or flesh in the body of the animal at the commencement of each hunger experiment might be placed in a lessening series in the order No. 3, No. 1, No. 2, No. 4, No. 5,—the results obtained by Bischof and Voit might fairly be interpreted as meaning that the amount of urea excreted per diem depends directly on the amount of nitrogenous material stored up in the animal as flesh. The contradiction between the two sets of observations, between the facts of Bidder and Schmidt's cat, and those of Bischof and Voit's dog, requires explanation; but unless there are serious errors in the actual determinations of the latter, it is difficult to escape from the conclusion that all the nitrogenous material taken in as food does become part and parcel of the body, is really assimilated into flesh (using that word in the general sense defined above, and not limiting it, as Bischof and Voit appear to do, to muscular tissue) before it undergoes metamorphosis into urea, and that one of the principal laws of nutrition is that the amount of metamorphosis of flesh, taking place in the body at a given time, depends directly upon, in other words is a function of, the amount of flesh therein present. The validity of this conclusion is assumed in all Bischof and Voit's subsequent investigations, and thus forms the basis of their other results, which are as follows. It will be remembered that these observers have left room for errors by not determining directly the carbon of the egesta. Their practice of always reckoning the nitrogenous material of the body as wet muscle only leads also in all probability to additional inaccuracies, and throughout the whole of their researches an element of uncertainty is introduced through variations in the nutritive power of the animal, both as regards character and amount, caused by the diet itself, and well seen when a change is made from one kind of food to another. Thus with the same rations, viz. 1,800 grms. meat, the dog on one occasion, after living for the previous forty days on bread, gained in bodily weight at the rate of less than 1 grm. per kil. per diem; at another time, after three days' hunger following an insufficient meat diet, he gained at the rate of over 2 grms. per kil. per diem; on a third occasion, after a long suspension of the experiment, during which he lived after the manner of dogs in general, he lost at the rate ·66 grm. per kil. per diem.

The first series of experiments were made with a diet of meat alone. The first and chief effect of meat taken as food, was a rise in the amount of urea, that is to say an increase in the metamorphosis of flesh. Supposing that at the time of giving the food, the dog was already ill-fed and losing in bodily weight, the effect of a small quantity of meat was such an increase in the metamorphosis, that the animal stored nothing up but continued to lose in weight. An increase of the meat ration similarly increased the metamorphosis and similarly permitted the loss in weight. A further increase acted in the same way. But this was observed, that with a succession of equal increments of food, the increments of metamorphosis successively diminished. Hence, by continuing the increase of food, a limit was at last reached, at which the increase of metamorphosis ceased. The animal might then be said to be in a condition of equilibrium, the ingesta and egesta balancing each other. Such a state of things was established in Bischof and Voit's dog only when the amount of meat consumed as food was equal to about $\frac{1}{20}$ to $\frac{1}{25}$ of the total weight of the animal. Beyond that point an increase of food was stored up as increase of bodily weight. But in a very short time after such a gain in weight, the totality of the processes of the economy accommodated themselves to the new state of things, to the increased mass, and thereby gave rise to an increase of metamorphosis. To supply this increase of metamorphosis a further increase of food was required, and so another equilibrium was established on a higher platform, so to speak, of waste. On still further addition, the same process was gone through again, until the animal refused to eat the required quantity of food. Loss of weight of course then occurred, with a reduction of the equilibrium to a lower level.

The cause of the successive diminution in the increments of metamorphosis caused by successive augments of the food, is to be sought for in the approximatively constant quantity of oxygen present in the blood for the purposes of oxidation. We have therefore three things to notice. First an amount of metamorphosis proper to the flesh. Secondly, an increase in metamorphosis due to the presence of food. Thirdly, a government of the metamorphosis by the oxygen of the system. In other words, the metamorphosis is a function of three factors—one, a constant (or approximatively such), the other two, variables—viz. Oxygen, Flesh, and Food, or as Bischof calls it, Plasma, Blastema. The next series of experiments was conducted with meat and fat, and with fat alone. It was found that the addition of fat to a meat diet affected the body in two different ways. On the one hand, fat not only did not prevent by its presence that increase of metamorphosis which had previously been observed to follow upon an increase in the quantity of meat consumed, but was itself a cause of increase, inasmuch as it added to the mass and internal labour of the economy. On the other hand, apparently from its greater readiness for oxidation, it preoccupied the oxygen of the system, and so sheltered the flesh from oxidation and metamorphosis. Hence the addition of fat to meat as food lowered the platform at which metamorphosis was arrested for want of oxygen and an equilibrium established. One third or one fourth only of a quantity of meat required for an equilibrium, when meat alone was given, was needed when fat was added to it.

Sugar and starch were found to act very much in the same way as fat, except that, apparently by reason of the greater facility for oxidation possessed by sugar, equilibrium was established with even a less expenditure of meat than was the case with fat. A similar conclusion may be drawn from the results of the system of Mr. Banting. The experiments of Henneberg and Stohmann on oxen, conducted in a very similar manner to those of Bischof and Voit, the carbon of the egesta being calculated, not directly determined, are interesting as showing that the herbivora are subject to the same laws of nutrition as the carnivora. These observers found that in the ox the metamorphosis was a function of the flesh; that it was increased with an increase of protein-substance in the food, the increment of the metamorphosis successively diminishing, however, with successive increase of protein food, so that at last an equilibrium was established; that the addition of non-nitrogenous material to the food lowered in proportion to its amount the quantity of protein-substance necessary for the establishment of that equilibrium or for the storing up of bodily weight. As might be expected, the amount of protein-substance necessary for an equilibrium under any circumstances was far less than that required by the dog.

Man, standing so to speak between carnivora and herbivora, has been studied by Ranke with very similar results (Ranke in many of his experiments directly determined the carbon of egesta in Pettenkofer's apparatus). He also found that the metamorphosis was a function of the flesh of the body, that it was also a function of the food or Blastema, being largely increased by a meat-diet. Contrary, however, to the experience touching the dog, he was unable to reach an equilibrium when feeding on meat alone. While eating the largest amount of meat possible, viz. 1,800 grms., he still lost weight. He moreover found that the addition of fat or starch to food, rendered easy the establishment of an equilibrium. The concordance of the results of these different observers speaks strongly for the probable correctness and worth of these "laws of nutrition."

In the above statement, metamorphosis generally, and metamorphosis of flesh, have been used indiscriminately on the ground that the latter is really the chief, central and determining part of the whole. It remains to determine how, when equilibrium has been established, and a storing up commenced, the elements of flesh, fat and water are distributed in the increase; similarly also how they are related to each other in a decrease when that occurs. The conclusions arrived at when the carbon was calculated, instead of being observed, must of course be received with caution.

According to Bischof and Voit, when an animal is ill-fed with meat, he loses not only flesh but also fat from his body. With an increasing diet of meat, and accompanying increase of metamorphosis, the loss of fat lessens, and finally ceases with the establishment of equilibrium. Pettenkofer and Voit have moreover shown that with a rich meat-diet, when there is a balance between the nitrogen of egesta and ingesta, there is most probably, judging from the retention of carbon, a very considerable storing up of fat. The same result was also arrived at by Bidder and Schmidt. It is only intelligible on the hypothesis that the metamorphosis of flesh, like Bidder and Schmidt's metamorphosis of blastema, consists in the splitting up of protein into a nitrogenous and a hydrocarbonous portion. Ranke, on the contrary, found that with the largest meat-diet possible, he still consumed fat while he stored up flesh, with a total result of loss in weight owing probably to a giving off of water. The addition of fat to food naturally lessened the consumption of the fat of the body, if in sufficient quantity, arrested it or even led to a storing up of fat. It was also found that when, with a given quantity of fat, the amount of meat-food was pushed beyond what was necessary for an equilibrium, and the flesh of the body consequently increased, with a proportionate increase of metamorphosis, such an excess of nitrogenous material undergoing metamorphosis was at last arrived at, that it preoccupied the oxygen of the system to the exclusion of the fat. The fat of the body was retained and that of the food stored up in presence of a large unnecessary nitrogenous metamorphosis. The same result was also obtained by Henneberg, and illustrates the uselessness of attempting to increase the casein of milk by giving protein-food beyond a certain limit. Bischof and Voit found sugar and starch also to spare the consumption of fat, but the dog was found unable to digest such a quantity of sugar as might be supposed sufficient to cover the total waste in fat and lead to a storing up of it. Henneberg however found that this was extremely easy in the ox, a fact which has been largely shown by the researches of Lawes and Gilbert. These last observers indeed found the storing up of fat to form so large a share of the total result of the general feeding of animals for the butcher, that they were led to consider butcher's meat in its totality not as nitrogenous but as hydrocarbonous food. Their results have a peculiar value inasmuch as they were obtained, not by calculating back from the excreta, but by the actual analysis of several typical specimens, and by numerous determinations of weight serving as data for comparisons. The effect of ordinary fattening food upon the flesh, fat and water of the bodies of oxen, sheep and pigs is illustrated by the following table:

*Calculated composition of* 100 *increase whilst fattening.*

| | Mineral matter. | Dry nitrogenous compounds. | Fat. | Total dry substance. |
|---|---|---|---|---|
| Average for 98 oxen . . . | 1·47 | 7·69 | 66·2 | 75·4 |
| Average for 348 sheep . . . | 2·34* | 7·13 | 70·4 | 79·9 |
| Average for 80 pigs . . . | 0·06 | 6·44 | 71·5 | 78·0 |
| A fat pig actually analysed . . | ·53 | 7·76 | 63·1 | 71·4 |

* Too high owing to foreign matters in wool.

The relation between the amount of metamorphosis, and consequently of the storing up or increase, and the various elements of the food, was thus found to be as follows. With sheep, the amount of dry nitrogenous material stored up in the body for every 100 pts. of the same consumed as food was on the average 4·41; of non-nitrogenous material, that is fat, stored up for every 100 pts. of non-nitrogenous substance consumed as food, the quantity was 9·4, the remainder in each case being either not digested, or lost in metamorphosis. With pigs the numbers were 7·34 and 21·2 respectively, the largeness of the numbers being due in part at least to the pigs' food being more digestible. The same facts may be placed in another light. Thus with sheep, for every 100 pts. of the total dry matter of food (mostly oil cake and clover) there were stored up ·72 of dry nitrogenous material, 7·13 of fat, and ·02 of mineral matter; 91·94 being lost in digestion or in metamorphosis. With pigs, feeding on bran, beans and meal, the numbers were 1·44, 15·81, ·02, 82·73 respectively. It is worthy of notice that these independent observations may be interpreted as agreeing very closely with the general results described above, namely that increase of nitrogen means increase of metamorphosis, and that an amount of nitrogen in fattening food beyond a certain limit does not end in storing up of flesh, but in an augmentation of nitrogenous metamorphosis with lessened waste of fat. That fat was actually formed in the body is clearly shown by the fact, that for 100 pts. of fat as such consumed in food, from 405–472 pts. of fat were stored up as increase. No marked difference was observable between sugar and starch as fat-storing constituents of food.

Bischof and Voit, experimenting with gelatin, found that a large addition of that substance to a meat-diet led to a storing up of flesh but a waste of fat, when the quantity of meat consumed with the gelatin was such that either with it alone or with fat besides there was no storing up of flesh. It was hence inferred that gelatin really does to a certain extent take part in the metamorphosis of flesh, and does not simply shelter the flesh by preoccupying the oxygen after the manner of fat. So large an amount of gelatin, however, was necessary for this purpose as to explain why animals fed on gelatin alone could not thrive.

Our knowledge of the history of each alimentary principle, as it passes through and among the metamorphoses sketched above, is necessarily very imperfect, and will be more fitly put in the way of question than of statement. What, for instance, is the history of sugar? Is it absorbed into the blood and at once, if required, oxidised? If the surplus is stored up as fat, how does it become fat? Is the fat which is stored up by reason of the presence of the surplus, really and truly that same sugar exchanged into fat, or did the sugar step into a metamorphosis, and by a sacrifice of itself turn off in fat certain elements which would otherwise have followed another path? Questions such as these pertaining to each alimentary principle spring up in abundance, but their solution belongs rather to physiology in general than to nutrition in particular. We may mention a few experiments only which seem to suggest that the complexity of the changes taking place in the economy is rather under than overrated in our present accepted doctrines.

It is well known from the experiments of Regnault and Reiset that the proportion of oxygen fixed in respiration which reappears with the carbonic acid of the egesta varies according to the food, being greater with the carbohydrates than with the hydrocarbons. Pettenkofer and Voit observed, however, that in their dog, when fed on flesh with sugar or starch, the amount of oxygen in the carbonic acid considerably (127 to 100) exceeded the total amount of oxygen fixed in respiration. This was coincident with the appearance of free hydrogen and marsh-gas in the respiration chamber. Guided by the investigation of Planer on intestinal gases, they came to the conclusion that the starch and sugar suffer within the alimentary canal a sort of fermentative decomposition, by which, as in vinous fermentation, a quantity of carbonic acid is given off, in the production of which the oxygen of the atmosphere has had no part. This observation shows strongly that the amount of carbonic acid in the egesta is no true measure of the oxidation of the body, and therefore of the generation of force, as has generally been supposed to be the case.

It is curious that Grouven, working through the devious and dangerous path of elaborate analyses and still more elaborate calculations, should have come to a very similar conclusion with regard to the fate of the carbohydrates consumed as food by oxen. He attempted to estimate the "nutritive value" of various alimentary principles, starch, sugar, gum, &c., &c., by mixing known quantities of them with a fixed ration of straw, and then, having calculated the changes that had taken place during a given time in the body of the animal, gain or loss of flesh, fat and water, compared the results with the previously determined effect of the straw-ration. He found that his facts only became intelligible on the hypothesis that within the alimentary canal the carbohydrates were split up into two sets of bodies, one rich, the other poor, in oxygen; that the former were thrown off unused, while the latter were absorbed and probably were converted into fat. He goes even so far as to deduce from his elementary calculations the formulæ of the change. Thus starch gave rise to glycerin, butyric, and lactic acids, which were assimilated, and carbonic acid and marsh-gas, which were at once excreted. These results are perhaps of more value as provocative of future researches than as being by themselves trustworthy facts; but at least they point to possibilities, both of digestion and nutrition, not as yet fully recognised.

The results described above as laws of nutrition refer to what have been called force-generators. The laws belonging to the force-regulators are so complex, so little understood at present, and consequently so much debated, that it is thought better to omit the consideration of them altogether.

Some substances, such as alcohol, can perhaps hardly be regarded as of settled position whether among the generators or regulators; others, tea, coffee, salt, &c., have likewise been the subjects of much research and debate. (See Smith, Voit, &c., &c.)

### B. *Dynamics.*

While the statical part of the subject is of course of most interest in reference to the nutrition of animals destined to be slaughtered for food, the dynamical part is of most importance when the nutrition of man is considered. What kind of food is best adapted for the development of muscular, what for nervous force? are the most fundamental problems of physiology. Previous to entering into detail, however, an inquiry should be made (if for nothing else, at least for the sake of justifying the assumption of the applicability of the conservation of forces to the living frame) between the total income and total expenditure of force. This will be most conveniently done by reducing both to units of heat. The determination of the total amount of force expended within a given time by an animal body is a comparatively easy task. For, diverse as are the various manifestations of force within the economy, they are all reduced, before they leave the body as expended force, into two modes only, namely heat and mechanical effect, the quantity leaving the body as electricity being probably exceedingly small. Thus all the various forces which we class together under the name of nervous force resolve themselves, after all their multitudinous wanderings and transformations, into heat, except the minute fraction which may be supposed to be carried on into muscular action, and so to find its exit as mechanical effort. Muscular action too loses itself partly as mechanical effect, but to a much greater amount probably as heat. All secretive or nutritive action again goes out as heat. Heat and mechanical movement are in fact the only true *effectus* of the animal body. Whatever does not go out in the one form, issues in the other. Two animals, living on the same food, and subject to the same metamorphosis, will rise to the same amount of actual energy, and yet in the one a large amount of that energy may assume the form of mechanical effect, while in the other, no muscular exertion being made, it nearly all goes out as mere heat, which, being dissipated as soon as generated, causes no alteration in the animal's temperature. Hence if we estimate the total mechanical effect of any animal during a given time, and the total amount of heat given off at the same time, we shall obtain the total amount of expended force. This may readily be done by placing an animal in a calorimeter, with a tread-wheel for determining the mechanical effect. By reducing the mechanical effect to units of heat, and adding them to the number of units of heat denoted by the calorimeter, we arrive at the total expended force estimated in units of heat. A calorimeter is doubtless not a proper home for an animal, and therefore probably the result of the experiment will not give accurately the normal expenditure of the natural animal, seeing how sensitive and responsive in all its parts is the animal economy to variations of temperature. Yet it cannot be far from the truth.

The estimation of the total force of the income is a much more difficult task. The units of heat given off by the combustion of each article of food have to be determined, and from their sum total has to be deducted the number of units of heat still obtainable from the incompletely oxidised portion of the excreta belonging properly to the food in question. Unfortunately this at present has not been accomplished. It has generally been deemed sufficient to calculate the latent energy of any alimentary substance from the units of heat given off by the combustion in an uncombined state of its carbon and free hydrogen. This however (see Heat) leads to a result which we may safely assume as being incorrect, without knowing how far it errs from the truth. Hence the failure of Dulong and Despretz to obtain a balance between the actual heat given off by an animal during a given time, and the amount calculated as due to the quantity of carbon and hydrogen presumed to have been actually oxidised in the system during that time, cannot be regarded as any argument against the possibility of obtaining such a balance with great exactitude if more correct methods were employed.

Using, however, such imperfect means in the absence of better ones, Helmholtz calculates that a man of 82 kilogrms. weight expends in 24 hours 2,700,000 units of heat, of which 2·6 per cent. goes to warming the food and drink, 2·6 per cent. to warming the air of respiration, 14·7 per cent. is lost in the evaporation of water through the lungs, the remainder 77·5 per cent. being distributed over loss by urine and fæces, evaporation from skin, radiation and conduction from surface, and mechanical effect.

Ludvig calculates the mechanical effect of a good day's work to be equivalent only to 220,930 units of heat.

Still more difficult is the task of tracing backwards to the food or onwards to the excreta, any of the special kinds of forces at work within the economy. To take for instance muscular force, as one of the simplest, it may be asked, which elements of food contribute solely or chiefly to its production, and which of the elements of the egesta may be taken as the index of its occurrence. The Rev. S. Haughton (Dublin Quarterly Medical Journal, 1859, 1860), taking it for granted that the nitrogen of the urine and fæces represented the whole muscular or mechanical, nervous or mental, and nutritive or vital, work of the economy, while the remaining excreta answered to what he calls the *opus calorificum*, made the following investigation. Having determined the daily excretion *per anum et vesicam* of nitrogen reckoned as urea in a series of men of different bodily weights, performing different mechanical work, undergoing different mental labour, he was enabled to construct a series of equations, which he solved for certain values which it was desired to know. He thus calculated that 300 grains of urea represent the daily nutritive work of a man weighing 150 lbs.; that 136·5 grains. of urea represent the muscular force required to lift 150 lbs. through one mile, a hard day's work; that 222 grains. of urea represent the daily mental exertion of a man of business. It need hardly be said, however, that the assumptions on which these calculations are based, are open to grave objections.

In dealing with the statics of this subject the word flesh was used to denote the total protein-substance of the body. And it was only in this wide sense of the word that urea was considered as the result of the metamorphosis of flesh. It is true that Bischof and Voit use the same word flesh as synomymous with muscle, but such an assumption rests on no basis of facts. Although the nervous system in Bidder and Schmidt and Chossat's experiments seemed to suffer but little waste in inanition, we cannot for that reason conclude that during life it suffers little metamorphosis. On the contrary, it is impossible, with the general views by which we are judging the whole subject, to think otherwise than that where there is apparently so much production of force, there should also be much change. And as far as the changes in the nervous tissue simplicate the protein substances therein contained, they must be considered as giving rise to urea. In the liver again, in the glands, and in all the other organs which we may call the nutritive organs, we must also (in addition to the changes supposed according to one theory to occur in the digested food as it passes through or comes in connection with those organs in the blood current) suppose considerable, it might almost be said, excessive metamorphosis to take place, which in so far as it is nitrogenous will also produce urea. Hence the total amount of urea cannot be taken as an index of the metamorphosis of muscular tissue only. Nor can we fairly assume that even a large part of it is to be so regarded. It may be urged that muscular tissue forms a large part of the total protein-substance of the body, that we have every reason to believe that it suffers great and rapid changes. But, we possess no exact information as to how large a share in its metamorphosis is taken by its nitrogenous constituents alone, and on the other hand we are similarly ignorant of the intensity of nitrogenous transformations in the other organs of the body. It is true that in muscular tissue we find creatine and creatinine, and there is some reason for believing that they (one or both) are increased during muscular contraction when metamorphosis is presumed to be increased; but the physiological connection between creatinine or creatine and urea has not yet been fully traced. On the contrary, there are not wanting facts indicating the closest bonds between urea and the liver. So marked indeed are they that the action of the liver has been called in to assist the theory of the luxus-consumption, on the idea that the changes taking place there belong not exactly to the liver itself, but to the blood in the liver. On these points, however, our information is exceedingly imperfect.

Physiologists perhaps err in being apt to regard the processes of the animal body as too simple, too straightforward. May not urea and carbonic acid be, not the result of a splitting up and facile oxidation, but the ends of a long series of, perhaps backward and forward changes, so that the point or place where each is first detected is not necessarily the place where the most important act of metamorphosis takes place?

If it is difficult to connect urea in any special manner with the metamorphosis of muscular tissue, it is still more difficult to connect it with the exhibition of muscular force. If urea were the most important product of muscular metamorphosis and muscular metamorphosis the most important source of urea, then since, during muscular contraction,

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the metamorphosis of muscular substance is presumed, on apparently satisfactory grounds, to be largely increased, the amount of urea also ought to be largely increased by muscular exertion. It is true that under this view there will always be in the urine a tolerably large constant quantity of urea due to the amount of muscular exertion employed in visceral movements, which varies only within comparatively narrow limits. But such an amount must be fully overpowered by an excess of urea due to violent and long continued exercise. Observations (Smith, Voit, Speck, Lehmann) on the effect of muscular exertion on the excretion of urea are not unanimous. Yet, even when allowance is made for retention, that is for decrease of elimination as compared with decrease of formation, the conclusion may fairly be drawn that exercise even carried to exhaustion produces an increase of urea too small to be regarded in any way as an equivalent of the expended muscular force. At the same time observers are equally agreed that muscular exertion does produce a very large increase in the carbonic acid of the egesta. So clearly did this come out in the experiments of Dr. E. Smith, that that gentleman believes himself justified in recommending an addition of carbon to the food when bodily exertion is called for. It has been urged that Voit and others, by simply estimating the urea (with uric acid, &c.) in their experiments, have left open the possibility of other nitrogenous bodies being present in large quantities on such occasions, and on such occasions only in the urine. But these hypothetical bodies have never been detected, and the possibility of their existence does not negative the fact of the increase in the carbonic acid. It must be remembered however that there is in the living muscle, even when perfectly at rest, an active metamorphosis still going on, resulting in part as electricity, but finally as heat. Perhaps even during the very act of contraction (as distinguished from the conditions *immediately* preceding and following) there is not so much an increase of metamorphosis as a change in the direction or form into which the energy set free by the metamorphosis is converted. If so the carbonic acid would be only indirectly, and the urea not at all, an index of the amount of expended force, while the total metamorphosis of the muscular system would measure possibilities of action rather than actual achievements. When we reflect that the animal body considered as a working machine is characterised by being subject to sudden calls for action from every quarter, it will be easily understood that the best state of preparation for emergencies is not one in which there is a mere store of latent energy, but one in which force is continually being liberated and therefore ready at a moment's notice to be turned in any particular direction, converted into any particular form. This of course implies that for every mechanical effect, a large amount of force is spent in a non-mechanical manner, and therefore apparently lost. But so abundant are the resources of the economy for the using up of this wasted force, that according to Helmholtz, while the best steam-engine loses nine-tenths of the total power of its fuel, the human body is able to convert into mechanical effect one-fifth of the total power of its food.

Urea then cannot be taken safely as a measure of mechanical work done by the body; with still less safety perhaps can it be taken as a measure of the mental work. And as it is impossible at present to trace the various members of the egesta back to the various forms of vital force, so it is impossible to trace the latter back to the various constituents of food. If one general view of the whole vital processes can be regarded as more likely than another, it is perhaps the idea that the brute force of the economy, so to speak, is represented by the carbon (and hydrogen) of its food, while the nitrogen is more closely concerned with internal changes by which that brute force is converted into the many varieties of vital energy.

Playfair argues that only the nitrogenous alimentary principles are concerned in the production of muscular (and mental?) force, and gives calculations showing that the latent energy of such an amount of albumin as is usually consumed by active labourers is sufficient to account for the actual force, both of the internal muscular movements and of the external 'useful work' of an ordinary man. But Carpenter has made calculations which lead to an exactly opposite conclusion; and Haughton's equations, as far as they can be trusted, tend to support the view that the force of muscular action is derived, in part at least, from the hydro-carbons or carbo-hydrates of food. So long as the present uncertainty about the latent energy of complex substances continues, and so long as the evolution of heat is not observed at the same time that the development of mechanical force is estimated, all questions of 'dynamics' must remain obscure.

The following works and memoirs may be consulted:

Barral, Statique chimique des Animaux, 1850.

Bidder und Schmidt, Die Verdauungsäfte und der Stoffwechsel, 1852.

Bischof und Voit, Die Gesetze der Ernährung des Fleischfressers, 1860, and their Critic.

Vogt, C., Moleschott's Untersuchungen, 1859.

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Carpenter, W., On the Mutual Relations of the Physical and Vital Forces, *Phil. Trans.* 1850, and *Quarterly Journal of Science*, 1864.

Gronven, Fütterungs-Versuche, 1864.

Hammond, Researches on Food, 1857.

Hildesheim, Die Normal Diät, 1856.

Henneberg und Stohmann, Fütterung der Wiederkaner, 1860.

Lawes and Gilbert, Composition of Animals slaughtered for Human Food, *Phil. Trans.* 1860, and numerous papers in the *Journal of the Royal Agricultural Society*.

Moleschott, Physiologie der Nahrungsmittel, 1859; also Kreislauf des Lebens.

Payen, Des Substances Alimentaires, 4th. ed 1865.

Parkes, Urine, 1860.

Pettenkofer u. Voit, Respiration. *Annalen der Chemie und Pharmacie*, 1863, Suppl. ii.

Playfair, The Food of Man in relation to his Useful Work, 1865.

Ranke, J., Kohlenstoff und Stickstoff-Ausscheidung der ruhenden Menschen. *Arch. f. Anat. u. Phys.* 1862.

Savory, Uses of Food, *Phil. Trans.* 1862.

Smith, E., Respiration, *Phil. Trans.* 1859; Urea, *Phil. Trans.* 1861. On the Food of the Labouring Classes. *Sixth Report of Medical Officer of Privy Council*, 1864; and other papers in *Brit. Assoc. Reports* and elsewhere.

Voit, Physiologisch-chemische Untersuchungen, 1857.

Ueber den Einfluss des Kochsalzes, des Kaffees und der Muskel bewegung auf den Stoffwechsel, 1860. Ueber den Stickstoff-Kreislauf im thierischen Organismus, *Ann. d. Chemie u. Pharm.* 1863, Suppl. ii.

M. F.

**NUTRITION OF PLANTS.**—The Nutrition of Plants, like that of Animals, may be studied in accordance with the doctrine of the Conservation of Force, in reference to the mutual relations of income, capital, and expenditure. At the first glance, however, a remarkable difference may be observed between the two kingdoms. In the case of animals, the income consists almost entirely of force associated with material as latent energy; in the case of plants, the income is composed to a preponderating extent of actual energy in the form of force derived directly from the sun, and of material associated with as small an amount as posible of latent energy. With animals there is such a large constant expenditure of force in the shape of actual energy, such a large concomitant waste of effete material that even in the case of those animals which are purposely fed with a view to increase of capital, that part of the income which is stored up from time to time as increase of material and latent energy, bears an exceedingly small proportion to that part which goes to swell the expenditure; with plants the amount both of force and material continually expended is so slight that by far the greater part of each accession of income is retained as increase of capital. With most animals the value of the capital depends almost entirely on the amount of actual energy it is able to supply when occasion demands; with nearly all plants the value of the capital is expressed almost exactly by the amount of latent energy its material represents. Animals are machines for the conversion of latent energy into various modes of actual force; plants are machines for converting the one actual force of the sun into various collections of latent energy. We may, using the while very general terms, speak of a circulation of force and material through the world. Light (heat), carbonic acid, water, and ammonia, enter into the vegetable kingdom, and reappear as protein; carbohydrates and oxygen enter the animal kingdom, and reappear as heat and mechanical effect on the one hand, and as carbonic acid, water, and ammonia (urea) on the other. In the third or inorganic kingdom, the carbonic acid, ammonia, heat, and mechanical effect are driven from their place of birth by distributive forces and scattered over the globe. Thence in turn the vegetable kingdom draws in part its income.

Such a distinction between the animal and vegetable world, though satisfactory as a broad generalisation, must not however be taken as strictly true. The one kind of life is not exactly the inverse of the other. On the contrary, in order to include all vital phenomena, we must imagine each to consist of two processes; the one destructive and resulting in the liberation of actual force, the other constructive and leading to the accumulation of latent energy. In the one life, one process is predominant; in the other, the other. Thus animals, while for the most part they absorb latent energy in the form of food and expend it chiefly as actual force, are yet at the same time engaged during the whole of their lives, in increasing and concentrating, so to speak, by particular applications of a portion of their total force, the amount of latent energy of some of the materials of their food through the process called assimilation. During the early stages of their existence, while they are growing, they do this to a very marked degree; and at some periods (incubation) they receive, and convert into temporary latent energy, a

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quantity of actual force in the shape of heat. So plants, though their chief function is to employ solar energy in decomposing carbonic acid and water with liberation of oxygen, and thus to construct elaborate compounds of carbon, hydrogen, nitrogen, and oxygen, as seats of latent energy, nevertheless from time to time consume those very compounds, absorbing oxygen, forming carbonic acid and giving off actual force in the shape of heat. For instance, during germination, flowering and fruiting, there is always oxidation going on, and even a considerable amount of heat thrown out; and during the whole life of a plant, those parts which are not green are always occupied in forming and exhaling carbonic acid, and those which are green behave in the same way when light is absent, so that the total amount of oxidation going on in a plant is very considerable. The income of plants consists partly of force, partly of material. Force is supplied almost entirely in the form of solar energy. Part of the energy so received may be considered as acting simply as heat, since, for the organic processes of vegetable as of animal life, a certain temperature is necessary. In the majority of animals, however, an internal source of heat renders the thermal influence of the sun of subordinate importance. Plants, on the other hand, are more directly dependent on solar warmth, their own caloric production being, as a whole, very limited. But by far the most important function of the solar energy received by plants is that peculiar one whereby sun-light, acting on the green or chlorophyll-containing organs, deoxidises carbonic acid and water, and thus enters as latent energy into the various vegetable organic compounds. As by the union of carbon and hydrogen with oxygen to form carbonic acid and water, a certain amount of actual energy is set free, so in the reverse process a corresponding amount of energy becomes latent. The latent energy possessed by vegetable products and exhibited through either combustion or alimentation is simply energy derived from the sun and appropriately converted during the life of the plant.

The materials of the income of a plant are derived partly from the soil, partly from the atmosphere.

Those bodies which are drawn from the soil are said to be absorbed by the roots. Into a mass of soil, the roots of a plant spread during its growth in various directions, and extract therefrom certain constituents by virtue of processes as yet not fully understood. This absorption has a "selective" character. One plant will absorb certain constituents in given proportions; another, the same constituents in different proportions or different constituents. So, out of a given mixture, a plant will by no means absorb to the largest extent those substances which are present in greatest abundance. Marine plants growing in a fluid containing a great excess of sodium, themselves contain a great excess of potash. Land plants contain but little aluminium, though that body exists in large quantities in most soils. Aquatic plants, whose soil is a fluid, of course absorb their soil-derived constituents from solutions. Land plants may also be made to do the same thing. Thus Stohmann (Ann. Ch. Pharm. cxxi. s. 285) grew maize-plants in pure saline solutions. It may fairly be presumed that all the bodies absorbed by the roots are in some way or other dissolved before they actually pass into the plant. Hence substances in order to be of any nutritive value must be capable of solution. But it does not follow that they must necessarily exist in a state of aqueous solution in the soil itself before they can be absorbed. On the contrary, ordinary soil seems to have a peculiar power of withdrawing saline materials from their aqueous solutions, and of retaining them in some peculiar physical combination with itself. And the experiments of Nageli and Zöller on the growth of beans in powdered turf saturated to a variable extent with saline matters, seem to show that saline nutritive elements are absorbed not directly from aqueous solutions percolating the earth, but indirectly through the agency of the soil.

Of the substances thus absorbed by the roots the so-called "mineral" matters form a large proportion. The most important and wide spread are potash, soda, lime, magnesia, and iron, with phosphoric, sulphuric, hydrochloric, and silicic acids. Less universal but still common are iodine, alumina, manganese. More rare, and probably in many cases accidental, are bromine, boron, copper, silver, zinc, lead, tin, cobalt, nickel, strontium, barium. To these may be added lithium, and some of the newly discovered metals. Water is of course absorbed from the soil.

Nitric acid and ammonia are also absorbed from the soil. These may have arisen from the decomposition of organic matters present in the soil as natural or artificial manures, or may have been brought down from the atmosphere by rain. It has been suggested (Völker, Cloez) that nitric acid is the particular shape in which nitrogenous material is absorbed by plants, all other nitrogenous substances (including ammonia) being reduced to that form, previous to absorption. There appears to be no evidence that organic nitrogen-compounds are absorbed as such except it be in the case of fungi and certain parasites.

Carbonic acid may be taken up from the soil. Lastly, there are in all soils representatives of the class of bodies known under the collective name of *humus*. It is

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generally thought that humus is not absorbed as such, but acts beneficially in a sort of preparatory manner on soils, by means of the acids arising from its decomposition. Rister however maintains that humus is absorbed and assimilated by plants.

The kind of material derived from the air is not the same under all circumstances. Under the action of light the green parts of the plants absorb carbonic acid; in darkness they cease to do so, taking up oxygen instead. Those parts which are not green absorb oxygen under all circumstances. That this absorption of oxygen is an act necessary to life is shown by the fact that plants kept in darkness (and therefore unable themselves to give out oxygen) in an atmosphere void of oxygen, perish.

It has been much debated whether plants absorb in any way nitrogen directly from the atmosphere. There appears to be no exact knowledge as to the power of plants to absorb combined nitrogen (ammonia, &c.) directly from the atmosphere, as distinguished from that obtained from the same source through the intermediate agency of the soil. As regards free nitrogen, Boussingault (Annales de Chim. et Phys. 1855, &c.) concluded from his experiments that there was no absorption. Ville and others maintain the contrary. Lawes and Gilbert (Phil. Trans. 1861; Chem. Soc. J. xvi. 100) support the views of Boussingault. The last-mentioned observers nevertheless state that the quantity of nitrogen brought down to the soil from the atmosphere by the annual rain will only account for a fraction of the nitrogen carried off by the annual crops, and infer that in the absence of nitrogenous manures there would seem to be some other as yet unnoticed source of nitrogen. Liebig (*Natural Laws of Husbandry*, ed. Blyth, 292) however maintains that the atmospheric nitric acid and ammonia are sufficient for ordinary vegetable purposes, and even that (through cultivation) an accumulation of nitrogen in the soil has taken place. The observation of Schönbein that nitrite of ammonia is produced during oxidation taking place in the atmosphere, has suggested a source of abundant supplies of nitrogenous food for plants.

The capital of a plant consists of the so-called vegetable products. The chief of these are protein-matters, cellulose, starch, dextrin, sugar, gum, pectin, chlorophyll, organic acids, fatty, waxy, resinous bodies, tannin, &c., &c. All these are so many collections of latent enegy, and available for food or fuel. They are nearly all of them present in every plant, and constitute the main part of the capital properly so understood. Besides these bodies, however, there are innumerable other compounds, of more or less frequent occurrence, possessing a greater or smaller amount of latent energy, some of them perhaps particular stages through which the material of the plant passes in its progressive metamorphoses, others most probably the products of a retrograde metamorphosis or off-shoots of either process. These last two kinds may fairly be brought under the designation of excretions, and ought therefore to be considered as the waste material of expenditure rather than as belonging rightfully to the capital.

One substance spoken of as protoplasm, a mixture of various nitrogenous and non-nitrogenous compounds, occurs largely in all growing parts, and may be regarded as a sort of middle term, to which a large part of the income tends and from which various items of capital arise.

Of the expenditure of a plant, a very limited amount consists of actual force. In the lowest forms of vegetable life locomotion is at times witnessed, and some of the higher plants exhibit occasional movements in their so-called irritable parts. In these cases a certain amount of force is lost as mechanical effect. And in all plants the act of growth, the transference and sustentation of material in various directions must be considered as an expenditure of mechanical force.

A constant but small loss of force in the form of evolved heat must also be admitted. Under ordinary circumstances this is almost insignificant; on certain occasions, however, it comes forward into great prominence. Thus in germination, a very considerable amount of heat is given out, and when many germinating seeds are collected in a heap, as in malting, the thermometer placed among them may rise to 110° F. During flowering also heat is evolved. In the spadices of the Arum tribe in particular the thermometer, it is said, will stand 20° or 30° F. above the temperature of the surrounding air. In all cases the evolution of heat is closely connected with the absorption of oxygen and the exhalation of carbonic acid.

Of the material thrown off by plants, besides water, the largest portion consists of oxygen given out by the green surfaces under the influence of light. A smaller portion consists of carbonic acid given off by the parts that are not green at all times and by the green parts in darkness.

According to Cloez (Ann. Sciences. Nat. Bot. [iv.] xx.) the yellow and red portions of particoloured leaves do not give off oxygen. The amount of carbonic acid exhaled in darkness is greater when the surrounding temperature is higher (Corenwinder, Ann. Scienc. Nat. Bot. [v.] 1, p. 297). During germination, flowering, and fruiting there is an increase in the excretion of carbonic acid. Saussure thought that considerable quantities of nitrogen were evolved by the leaves of plants while carbonic acid was being decomposed;

and **Draper** came to the same conclusion. But **Boussingault** (Ann. Scienc. Nat. Bot. [iv.] xvi.) maintains that such is not the case, having found reason to believe that the leaves of plants (at least of submerged plants) in sunshine give off appreciable quantities of carbonic oxide and marsh-gas. **Cloez** however, who with **Gratiolet** (*ibid.* [iii.] xxxii.) had previously found decided quantities of nitrogen to be exhaled by the leaves of the *Potamogeton perfoliatus*, reasserts (*ibid.* [iv.] xx.) the fact of the exhalation of nitrogen, and denies the excretion of carbonic oxide. The observations of **Lawes** and **Gilbert** oppose, as far as they go, the idea of nitrogen being exhaled. Many plants give off minute quantities of volatile hydrocarbons in the form of odours. To the action of these emanations, the presence of ozone in the neighbourhood of plants has been attributed.

It has been much debated whether or no, or to what extent, matters are excreted by the roots of plants. The beneficial or injurious effects which the growth of certain crops seems to exert on the vegetation of other crops, subsequently grown on the same ground, have been attributed to an accumulation in the soil of matters excreted by the roots of the first crops. Most of these facts, however, may be otherwise explained. Direct experiments have led to contradictory results, and those which seem to affirm the existence of an excretive function have been explained away by supposing the roots in such cases to have been injured. **Cauvet** (Ann. Scienc. Nat. Bot. [iv.] xv.) decides that the roots of plants, when sound, do not throw off any part of either poisonous or innocuous substances taken in by the plant in any way.

The class of Fungi and the leafless Parasites differ materially in their vital phenomena from other plants, and in some respects closely resemble animals. They receive little or no solar energy; they do not consume carbonic acid; they do not give off oxygen; they do not live on simple compounds of carbon and of nitrogen. On the contrary, they live either on decomposing organic matter or on the elaborated juices of plants, and they absorb oxygen from the atmosphere, giving back carbonic acid in return. They differ from animals inasmuch as they expend but little force either in movement or as heat. The force they absorb in their nutriment still remains for the most part within their bodies as latent energy. Hence the rapid growth of many of them.

It is evidently not within our present powers to draw a balance between the amount of force received by a plant as income on the one hand, and the latent energy possessed by the plant itself plus the fraction expended during its life-time on the other. This only is clear, that the solar energy is more than sufficient to account for the vegetable power. **Helmholtz** (Lectures Med. Gaz. 1864, i. p. 499), making a comparison between the total amount of solar energy falling on an acre of ground during the year, and the amount of force derivable from the plants grown on that acre during the same time, finds the latter only $\frac{1}{1477}$th part of the former.

The obstacles attending any attempt to draw a balance of material are also much greater than is the case with animals, since, in addition to atmospheric difficulties, trouble is met with in the fact that a plant, in order to flourish naturally, must be placed in a soil of a most complex character, out of which it extracts only a small portion for its own use. But such a balance, though wholly necessary for the purpose of investigating the nutrition of animals, is almost superfluous in the case of plants, since with the latter a different method of observation may be adopted. Instead of inferring the state of the capital from a comparison between income and waste, we can in dealing with plants, make a direct analysis of the capital, and so determine the variations it from time to time suffers through changes in the income; for those plants, concerning whose nutrition knowledge is most desirable, being generally grown in crops, a sufficient number of specimens can always readily be taken for examination.

The income may be roughly considered as consisting of three chief factors, solar energy, carbonic acid, and soil materials (including, as aqueous soil, the water in which aquatic plants live), and the process of nutrition as a function of all three. The total failure of any one of the three entails a speedy death; the comparative failure diminishes growth; increase of any one of the three augments the nutrition of the plant within certain limits. The accumulation of vegetable products of all kinds is dependent upon each and all of these factors. Thus the presence of carbonic acid is necessary for the development not only of carbon, but also of nitrogen-compounds, and inversely the amount of carbo-hydrates stored up by a plant will depend upon the nitrogen as well as the carbon of its food.

Seeing that plants are, in a broad sense, store-houses of carbon, the importance of carbonic acid (whether derived from air or soil) as a factor of nutrition cannot be overlooked. Plants entirely deprived of carbonic acid cease to live, while an increase of that body increases vegetation. A limit however to the beneficial results of increasing the carbonic acid of the atmosphere surrounding plants is soon reached, since oxygen also is a necessary element of vegetable life, and to the respiration, as it has been called, of plants as to that of animals, more than a certain percentage of carbonic acid in the air is injurious. The presence of light is absolutely essential to the accumulation of fresh material in the body of a plant. In its absence the oxidising processes become prominent and a certain amount of morphological change and even chemical transformation of material can take place. This is very well shown by the experiments of **Boussingault** (Ann. Sc. Nat. [v.] i. p. 314) on beans grown on a prepared soil in light and in darkness. In the light, a seed weighing ·922 grm. grew in 25 days to a plant whose dry weight was 1·293 grm., showing an increase of ·371 grm. which consisted of ·1926 grm. carbon, ·02 grm. hydrogen, and ·1591 oxygen. In the dark a seed weighing ·926 grm. grew in the same time and under the same conditions, except those of light, to a plant weighing when dried, ·566 grm., showing a loss of ·360 grm., which consisted of ·1598 carbon, ·0232 hydrogen, ·1766 oxygen. In the light there was a storing up of the elements of carbonic acid and water; in the dark a waste of the same. In the light the deoxidising or purely vegetable process was predominant; in the dark the oxidising or purely animal process. The latter supplied the force requisite for the partial development of the plant. The nature of the chemical transformations taking place in darkness is shown by the following composition of beans and bean plants after 21 days' growth in darkness:

| Seed. | Total weight. | Starch. | Sugar. | Cellulose. | Oil. | Nitrogenous matter. | Mineral matter. |
|---|---|---|---|---|---|---|---|
| Seed . . | 8·636 | 6·386 | . . | ·516 | ·463 | ·880 | ·156 |
| Plant (dried). | 4·529 | ·777 | ·953 | 1·316 | ·150 | ·880 | ·156 |

There was therefore a production of cellulose out of starch during darkness. The influence of the absence or presence of light on the development of various vegetable products, particularly of those which may be regarded as retained excretions, such as the alkaloïds, is well known. Boussingault regards the asparagine which is accumulated in beans growing in darkness as the vegetable physiological analogue of the animal urea.

The soil-materials may be divided into the "nitrogenous" and "mineral." Nitrogen is an essential element in the food of plants, and as we have seen, is probably derived from the soil. Though the quantity of it present in the seed may in many cases serve for the purposes of nutrition until the plant has arrived at a considerable bulk and accumulated a large stock of carbon-compounds, a limit is at last reached beyond which, without a further supply of nitrogen, no further growth can take place. This is very well shown by the experiments of **Stohmann** (*loc. cit.*) and of **Lawes** and **Gilbert** (*loc. cit.*). The results of the last observers show a very close connection between the presence of nitrogenous bodies (ammonia) in the soil and the accumulation in the plant not only of nitrogen but also of carbon-compounds. The increase in carbohydrates is however by no means proportionate to the gain in nitrogen. A large amount of the former is very often amassed by means of a very small quantity of the latter. In animals nitrogen is always in the foreground, and is, so to speak, the guide and governor of the total metamorphosis; in plants nitrogen is in the back-ground, and is, as far as quantity is concerned, the meanest of the factors of nutrition.

"Mineral matters," on the contrary, while they hold a very subordinate position as food-elements in the case of animals, are of primary importance for the nutrition of plants. Their influence is very clearly shown by growing a plant in distilled water or prepared soil. For a while there may be observed a growth consisting partly in the transformation of the contents of the seed and partly in the storing up of new material through the agency of the unoccupied mineral matter there accumulated; but, as soon as these are exhausted, no new stuff is formed and the plant thereupon speedily perishes. All plants have not the same mineral constituents, each species seeming to make a qualitative and quantitative selection from the soil of material best fitted for its welfare. So fundamental is this law that plants are often spoken of as lime-plants, silicious plants, potash-plants, &c. And **Stohmann** (*loc. cit.*) has shown by direct experiments that, in the case of maize for instance, all the mineral food elements have an independent value, that potash cannot supply the place of soda, nor magnesia that of lime, nor lime that of magnesia. But, though all the mineral constituents of a plant are necessary for its growth, they are not all of equal value as factors of nutrition. The ashes of a plant are not, like the skeleton of an animal, merely the framework of its body; minerals are not absorbed from the soil simply for the purpose of building up such a framework. On the contrary, they are closely interwoven with and intimately connected with the formation of organic compounds, and their chief function in the vegetable economy is to assist in the construction of those compounds. In other words, the growth of a plant, that is more particularly the manufacture of vegetable products, is a function of its mineral food elements. Some of these minerals are more active in this way than others, and certain elements are especially associated with certain products. Thus there is reason to believe that the alkalis are peculiarly connected with the formation of the carbohydrates, phosphates with that of protein matters, &c. That is to say, an increased absorption or assimilation of alkalis is equivalent to an increased formation of carbohydrates, &c. In the case of some other minerals, no such connection can be traced. Thus Sachs found that maize, which generally contains 18·25 per cent. of silica in its ash, would when debarred from the same attain its usual height and bulk, and bear seeds capable of germination with only ·7 per cent.

Inasmuch as the oxidising and destructive portion of vegetable life is quite as essential to the growth and welfare of a plant as the deoxidising portion which more directly leads to the storing up of material, oxygen must also be considered as a factor of the nutrition of plants.

All these factors are absolutely essential, though, as has been said, of unequal value. The effects of increments of each placed at the disposal of a plant will be limited partly by the nature of the factor itself, and partly by the disposition of other factors. Thus increase of "minerals" may in certain cases prove effectual far beyond any increase in "nitrogenous matters," but the effect will depend most closely on the amount of carbonic acid and solar energy available for use. So carbonic acid and solar energy are limited in their usefulness by the absence of soil-materials. Practically speaking, however, the carbonic acid of the atmosphere and solar energy are beyond the control of man. Consequently the nutrition of plants is modified by him through variations in soil-materials. (See Manures.)

The series of changes through which the inorganic elements of the food pass into the organic vegetable products are very imperfectly known. The non-nitrogenous products probably behave as follows. The mineral matters and water absorbed by the roots pass upwards as crude sap into the leaves and other chlorophyll-containing organs. Here, under the influence of the solar rays, they mingle with carbonic acid derived from the atmosphere, and processes are set up which result in the liberation of a certain quantity of oxygen and the detention of carbon and hydrogen as constituents of certain organic compounds. These resulting compounds may be either deposited in the leaves as starch, &c., or pass to other parts of the plant as nutritious elaborated sap, to be deposited or consumed as occasion demands. The presence of chlorophyll seems to be essential to the accomplishment of the metamorphosis. Thus, when a seed is allowed to germinate in the dark, a limited growth takes place, as the result not of any formation of new material, but of a transplantation of the old. No chlorophyll is produced, no starch; no carbonic acid is absorbed, no oxygen liberated. When all the protein substance, starch, &c. of the seed has been transplanted into the stem and leaves and deposited there as protoplasm, cellulose, &c., the plant perishes for lack of food. If, however, before that occurs, it be exposed to light, certain granules of chlorophyll, previously deposited in the protoplasm of some of the leaf-cells and possessing a yellow colour, gradually become green. If the light be insufficient, no progress is made beyond this stage, and the plant in this case too perishes by starvation. With more light starch is formed in the chlorophyll, and the plant lives and flourishes. Since only in the parts where chlorophyll exists is carbonic acid absorbed and oxygen liberated, and since only when there is chlorophyll somewhere in the plant is there any formation of starch at all, it seems reasonable to suppose that the presence of chlorophyll is essential to the construction of starch, and that when starch accumulates in any part free from chlorophyll, it has been carried thither from elsewhere, not generated on the spot. The fact that the green (chlorophyllic) parts of plants absorb the so-called actinic rays of the spectrum, has been considered a proof that these rays alone contribute the force required for the liberation of oxygen from the carbonic acid. Draper and Dauheny, however, maintain from direct experiments that only or chiefly the luminous rays are concerned in the process. And it is uncertain to what part of the spectrum is due the change to green chlorophyll from its yellow or uncoloured antecedents, and whether particular rays have any influence in determining the formation of particular varieties of the carbohydrates and other compounds.

Opinions concerning the share taken in the deoxidising process by the mineral constituents and the exact stages passed through by the carbon are purely theoretical. It is unknown whether the oxygen arises from a direct cleaving of the carbonic acid or whether it is thrown off at the end of, or by fractions in the course of, a long series of changes. It has been suggested that the carbohydrates may be formed by the carbon passing through a series of acids of increasing carbon-power for which the alkalis, &c. (apparently so closely connected with the carbohydrates) serve as bases.

The observations of Lawes and Gilhert (Phil. Trans. 1861, ii. p. 493) show the great rapidity with which carbonic acid is reduced in the light, and oxygen consumed in the dark, and support the opinion that "there can be little or no oxygen in the living cells of plants during the night or during cloudy days." They also suggest the "idea that there may be during exposure to light, in the outer cells which are penetrated by the sun's rays, a reduction of carbonic acid with fixation of carbon and evolution of oxygen, at the same time that in the deeper cells there is taking place the converse process of oxidation of carbon and formation of carbonic acid." In such case the oxygen of the outer cells would pass inwards, oxidising the more deeply deposited carbon compounds, while the carbonic acid of the inner cells would pass outwards to be there reduced.

Some writers attribute much importance to the fact of many elements being set free during the organic changes in a "nascent condition."

The career of the nitrogenous elements of the plants' food is also obscure. It has been supposed that the nitric acid and ammonia absorbed by the roots pass with the rest of the mineral constituents up to the leaves, and are there elaborated into protein compounds which either remain as parts of the leaves or become factors of the nutritious sap. A large portion of the nitrogenous material of a growing plant will be found in the form of a constituent of the so-called protoplasm, the semi-fluid occupant of the vegetable cell. In the vitalistic theories this protoplasm is endued with a plastic force, a power of moulding the form proper to the plant, and is sometimes spoken of as presiding over the nutritive changes.

The changes through which ammonia or nitric acid, with sulphuric or phosphoric acid, assumes the form of protein-substance are wholly unknown.

The nutritive processes of a plant are not the same, nor is its composition identical at all epochs of its life. Young plants are rich in alkalis, old ones in earthy and metallic oxides (Garreau, Ann. Sc. Nat. [4] xiii.—Corenwinder, *ibid.* xiv.). The "active principles" elaborated by certain plants often appear at particular ages only. The phenomena of "migration" play a very important part during the whole of the plant's existence. Thus, during germination, the protein matter or *aleuron* of the seed becomes liquefied and the starch is converted into dextrin, and perhaps into sugar with evolution of carbonic acid. The semi-liquid mass formed by the mixture of these bodies then migrates into the growing cotyledons, stem and root, or rather forms them by the extension of itself through chemical and morphological changes resulting in the building up of cellulose and cells. There is no loss of protein-matter during this transaction, but the sum of the starch, dextrin, sugar and cellulose of the plant are together less than the starch of the original seed. Solar energy, carbonic acid, and soil-materials being present, new material is constructed and growth proceeds. As the leaves wither and die, a certain amount of material, namely the protoplasm, is withdrawn from them and migrates to the still living organs. Hence, dead leaves consist mostly of cellulose with certain other matters peculiarly connected with that substance, protein, starch, and sugar, alkalis, and phosphoric acid, being left in exceedingly small quantities. As life advances, growth will for a certain time take place chiefly in the leaves as distinguished from the roots. Thus Anderson found that in turnips growing from July 7 to August 11, the leaves increased more than four times as fast as the roots. At a later epoch the process is reversed. In turnips growing from August 11 to September 1, the roots increased nearly twice as fast as the leaves. That is to say, of the material elaborated by the leaves, a very large proportion did not remain in those organs but migrated to the roots. In turnips growing from September 1 to October 5, the leaves were found to have decreased in weight, some leaves in fact had withered and fallen off, but the roots had vastly increased. In other words, the migration from the leaves to the root had been very active, the latter organs acting as storehouses for the stuffs constructed in the former. Further on in life another change takes place. The material amassed in the root migrates once more into the leaves, when these are formed again with the return of warmth. Finally, the plant flowers and seeds, material is withdrawn from both leaves and root, takes its last migration, and finds its last resting-place in its first starting-place, the albumen of the seed; the dead leaves and stem representing very little more than so much cellulose. A very similar migration may be traced in the storing up of starch in the tuber of the potato, in the stem of the palm, and in a multitude of other instances. The history of the metamorphosis and migration of material in olives has been traced by De Luca (Ann. Sc. Nat. (iv.), xviii.). Mannite appears in the young olive leaves at first in very small quantities, but increases in amount as development proceeds until the epoch of flowering, when it begins to diminish. By the time the leaves are withered it has nearly disappeared. It is also found in young flowers, but disappears as they reach perfection. It occurs, too, in the unripe fruit, but gives place to oil during maturation. A very close connection is observed between chlorophyll and mannite on the one hand, and between mannite and oil on the other, the mode of the development of the latter being thus indicated. M. F.

**NUTTALITE.** Syn. with SCAPOLITE.

**NUX VOMICA.** See STRYCHNOS.

**NYMPHÆA.** The ash of the leaves and stalks of *Nymphæa alba* and *N. lutea* has been analysed by Schnlz-Fleeth (Pogg. Ann. lxxxiv. 80):—

| | $K^2O$. | $Na^2O$. | $Ca^2O$. | $Mg^2O$. | $Fe^4O^3$. | $SO^3$. | $SiO^2$. | $CO^2$. | $P^2O^5$. | KCl. | NaCl. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N. lutea*: young leaves and stalks | 22·92 | — | 25·24 | 5·09 | 0·24 | 1·86 | 0·81 | 22·23 | 7·18 | 7·88 | 2·78 | = 96·23 |
| *N. lutea*: old leaves | 17·91 | — | 30·00 | 3·61 | 0·16 | 1·39 | 1·16 | 28·26 | 4·65 | 4·88 | 7·38 | = 99·35 |
| *N. alba*: leaves and stalks. | 14·41 | 4·48 | 18·89 | 2·67 | 0·25 | 1·21 | 0·49 | 22·16 | 2·58 | — | 29·66 | = 86·80 |

The young leaves and stalks of *N. lutea* yielded, after drying, 7·96 per cent. ash, the old leaves of the same 10·15 per cent., and the leaves and stalks of *N. alba* 12·99 per cent.

# O.

**OATS.** See CEREALS (i. 823).

**OBSIDIAN and PUMICE.** Obsidian is a glassy modification of felspathic or trachytic lava. Pumice is a porous, fibrous, capillary or tumefied mass, produced by the operation of various external agencies, chiefly aqueous vapour and a certain temperature in these lavas while in the fluid state. Many obsidians, when ignited in lumps, become brightly incandescent, and swell up to a tumefied mass of pumice, which, according to Abich, is more like natural pumice in proportion as the mineral contains less silica and more alkali. Pulverised obsidian does not exhibit these phenomena, but merely turns brown. Obsidians heated above the point at which the formation of pumice takes place, melt to a greenish glass. Similar glasses are also formed by the natural fusion of pumice. Both pumice and obsidian appear to be but little attacked by acids.

These minerals may be divided into two groups:—A. Those in which the silica amounts to about 60 per cent., less therefore than in glassy felspar (ii. 620); the pumices belonging to this group are tumefied, and have a dirty white or grey-green colour.—B. Those in which the silica amounts to 70–80 per cent.; the pumices belonging to this division are fibro-capillary, white, and have a silky lustre.

*a.* Obsidian from Teneriffe: specific gravity 2·528 (Abich, Geolog. Unters. p. 62). —*b.* Pumice from the same: specific gravity 2·477 (Abich).—*c.* Pumice from the Phlegræan Fields: specific gravity 2·411 (Abich).—*d.* Pumice from Llactacnnga, at the foot of Cotopaxi (Abich).—*e.* Obsidian from Lipari: specific gravity 2·370.—*f.* Pumice from the same: specific gravity 2·77 (Abich).—*g.* Obsidian porphyry from the greater Ararat (Abich).—*h.* Obsidian from Moldavia, Bohemia (v. Haner, Jahrb. Geol. Reichsaust, v. 868).

| | With about 60 per cent. silica. | | | With 70 80 per cent. silica. | | | | |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* |
| Silica | 61·18 | 62·25 | 62·04 | 73·77 | 74·05 | 73·70 | 77·60 | 79·12 |
| Alumina | 19·05 | 16·43 | 16·55 | 10·83 | 12·97 | 12·27 | 11·79 | 11·36 |
| Ferric oxide | 4·22 | 4·26 | 4·43 $Fe^2O$ | 1·80 | 2·73 | 2·31 | 2·17 | 2·64 |
| Manganic oxide | 0·33 | 0·23 | | | | | | |
| Lime | 0·59 | 0·62 | 1·31 | 1·21 | 0·12 | 0·65 | 1·40 | 4·45 |
| Magnesia | 0·19 | 0·79 | 0·72 | 1·30 | 0·28 | 0·29 | — | 1·48 |
| Soda | 10·63 | 11·25 | 6·39 | 4·29 | 4·15 | 4·52 | 4·21 | 1·21 |
| Potash | 3·50 | 2·97 | 3·66 | 3·90 | 5·11 | 4·73 | 2·30 | |
| Chlorine | 0·30 | 0·53 | 3·84 | 2·85 | 0·31 | 0·31 | | |
| Water | 0·04 | | | | 0·22 | 1·22 | | |
| | 100·03 | 99·33 | 98·94 | 99·95 | 99·94 | 100·00 | 99·47 | 100·26 |

The close agreement between the analyses of obsidian and pumice from the same locality, for example *a*, *b* and *e*, *f*, shows that the two are merely modifications of the same mineral.

The analyses show also that obsidian and pumice consist mainly of felspathic substance; they always, however, contain small quantities of earths, and iron-oxides, indicating an admixture of augite, olivin and magnetic iron ore. The obsidian and pumice of Teneriffe (*a*, *b*) consist almost entirely of oligoclase, which mineral likewise occurs pure in the midst of them. The pumice of the Phlegræan fields (*c*), also that of Ischia, Procida, and the volcano of Arequipa in Bolivia, which contain but little more than 60 per cent. silica, also consist mainly of oligoclase more or less pure. The minerals of the division B, which contain a rather large proportion of potash, appear to be mixtures of free silica with oligoclase and glassy felspar (ii. 620). The water in pumice is merely hygroscopic. The small quantities of chlorine are present as chloride of sodium or chloride of ammonium, which salts are frequently found in and upon lava.

The pumice from the neighbourhood of Lake Laach, analysed by Schaffer, exhibits a composition different from the preceding, containing only about 50–58 per cent. silica; and two specimens of obsidian from the great volcano of Hawaii differ still more in composition therefrom. A capillary variety yielded 51·19 per cent. silica, 30·26 ferrous oxide, and 18·16 magnesia (= 99·61); a glassy variety, 39·74 silica, 10·55 alumina, 22·29 ferrous oxide, 2·74 lime, 2·40 magnesia, 21·62 soda, and 0·33 water (= 99·67). The former appears to be an augite, $(Mg; Fe)^2SiO^3$; the latter is also probably an augite, but with an unusually large quantity of soda. (Rammelsberg's *Mineralchemie*, p. 637.)

**OCHRAN.** A variety of bole from Orawicza in the Bannat, containing 31·3 per cent. silica, 43·0 alumina, 1·2 ferric oxide, and 21·0 water. (Kersten.)

**OCHRE.** A term applied to many metallic oxides occuring in an earthy or pulverulent form: *e. g.* iron or red ochre, or molybdic ochre, &c.

**OCHROITE.** An impure cerite mixed with quartz, analysed by Klaproth.

**OCHOTA OIL** or **CAMPHOR.** Syn. with Laurin or Bay-berry Camphor (iii. 476).

**OCTAHEDRITE.** Syn. with Anatase (i. 289).

**OCTYL.** *Capryl.* $C^8H^{17}$.—The eighth alcohol-radicle of the series $C^nH^{2n+1}$. According to Bouis (Compt. rend. xxxviii, 735) it may be separated from the chloride, $C^8H^{17}Cl$, by the acetate of sodium in the cold. In the free state it is represented by the formula $C^{16}H^{34}$ (see Alcohol-radicles, i. 96), and is isomeric, or perhaps identical with hydride of cetyl, $C^{16}H^{33}.H$ (see Hydrides, iii. 182).

**OCTYL, BROMIDE OF.** $C^8H^{17}Br$.—Obtained by treating octylic alcohol with bromine and phosphorus. It is an oily liquid, smelling like the chloride, heavier than water, insoluble in water, soluble in alcohol. It boils with decomposition at 190°, and leaves a carbonaceous residue when distilled; burns with a smoky green-edged flame. It is decomposed by potash, yielding bromide of potassium and octylic alcohol, and precipitates silver-salts in alcoholic solution, but more slowly than the iodide.

**OCTYL, CHLORIDE OF.** $C^8H^{17}Cl$.—Produced: 1. By the action of hydrochloric acid or pentachloride of phosphorus on octylic alcohol (Bouis, Ann. Ch. Phys. [3] xliv. 128).—2. By that of hydrochloric acid upon octylene (Berthelot, Ann. Ch. Pharm. civ. 185).—3. By the action of chlorine on hydride of octyl (Schorlemmer, Chem. Soc. J. xv. 419); at the boiling heat (Wurtz, Jahresb. 1863, p. 509) at 40°–50°, avoiding an excess of chlorine (Pelouze and Cahours, Ann. Ch. Pharm. cxxix. 91). It is a colourless liquid, lighter than water, and smelling like oranges. Specific gravity 0·892 at 18° (Schorlemmer); 0·895 at 16° (Pelouze and Cahours). Boils at 175° (Bouis); at 170°—172° (Schorlemmer); 168°—172° (Pelouze and Cahours); at 162°—167° (Wurtz). It burns with a smoky green-edged flame, forming hydrochloric acid; does not precipitate silver-salts; is decomposed by potassium or sodium in the cold, yielding octyl [or hydride of cetyl] $C^{16}H^{34}$; but when it is heated with sodium the metal assumes a violet colour, hydrogen is evolved; and if the distilled liquid be repeatedly distilled with sodium till all the chlorine is removed from it, the product ultimately obtained is octylene $C^8H^{16}$ (Bouis). Chloride of octyl prepared from the hydride exhibits the same reaction as that obtained from the alcohol; when heated with alcohol and acetate of potassium, it is resolved into octylene and octylic acetate. (Pelouze and Cahours.)

**OCTYL, HYDRATE OF.** *Octylic Alcohol. Caprylic Alcohol.* $C^8H^{17}.H.O$.—This alcohol is obtained, according to Bouis and other chemists, by distilling ricinoleate of potassium or sodium with excess of caustic alkali. Others again assert that the volatile products of this reaction are heptylic alcohol, $C^7H^{16}O$, and methyl-œnanthyl, $C^8H^{16}O$. These opposite views have already been discussed in connection with heptylic alcohol (iii. 144). As there observed, we must suppose, pending the further investigation of the subject, that one or the other of these alcohols is produced, according to the particular circumstances of the reaction. The mode of preparation has been already described (*loc. cit.*). According to Limpricht (Ann. Ch. Pharm. xciii. 242), the separation of the methyl-œnanthyl formed at the same time, is never completely effected by means of acid sulphite of sodium, on account of the greasy nature of the compound formed; and the only way of effectually removing this acetone is that adopted by Bouis, which consists in repeatedly distilling the liquid over fresh lumps of caustic potash as long as any brown substance remains in the residue.

Octylic alcohol is also produced by distilling acetate of octyl (obtained from American petroleum) with potash. (Pelouze and Cahours, *loc. cit.*)

Octylic alcohol is a colourless transparent oily liquid, having a strong aromatic odour and making grease-spots on paper. It has no action on polarised light (Bouis). It boils at 180° (Bouis); at 179° (Moschnin, Squire); at 180°—184° (Pelouze and Cahours). Specific gravity = 0·823 at 17° (Bouis); 0·826 at 16° (Pelouze and Cahours). Vapour-density obs. = 4·55 (Bouis); calc. = 4·51. Its composition is as follows:*

| | Calculated. | | Bouis. | Moschnin. | Dachauer. |
|---|---|---|---|---|---|
| $C^8$ | 96 | 73·84 | 73·46 | 73·64 | 73·8 |
| $H^{18}$ | 18 | 13·84 | 13·88 | 13·8 | 13·9 |
| O | 16 | 12·32 | 12·66 | 12·56 | 12·3 |
| $C^8H^{18}O$ | 130 | 100·00 | 100·00 | 100·00 | 100·0 |

Dachauer, by dissolving sodium in the alcohol (purified by treatment with acid sulphite of sodium) and treating the resulting mass with chloride of acetyl. obtained acetate of octyl containing 70·0 per cent. carbon, and 11·9 hydrogen, the formula $C^2H^3(C^8H^{17})O^2$ requiring 69·7 carbon, and 11·6 hydrogen.

Octylic alcohol is insoluble in *water*, but dissolves in *alcohol*, *ether*, and *wood-spirit*, and very readily in *acetic acid*. It dissolves *phosphorus*, *sulphur*, *iodine*, fused *chloride of zinc*, *fats*, *resins*, and *copal*. It rapidly absorbs *hydrochloric acid* gas, which however it gives off again when heated. It combines with *chloride of calcium*, forming very deliquescent prisms, which dissolve in cold more freely than in hot octylic alcohol, and are decomposed by water. (Bouis.)

Octylic alcohol, when free from methyl-œnanthyl, is not altered by exposure to the *air*, or by passing oxygen through it at the boiling heat (Bouis). It is oxidised by *nitric acid*, yielding various fatty acids. *Sulphuric acid* dissolves in it, forming octyl-sulphuric acid, and generally also octylene and neutral octylic sulphate. By *fuming sulphuric acid* it is converted, first into octyl-sulphuric acid, then, on further action, into meta-octylene (Bouis). Fused *chloride of zinc* converts it into octylene. With glacial *phosphoric acid* it yields octyl-phosphoric acid. With *hydrochloric acid*, *pentachloride of phosphorus*, *bromine and phosphorus*, and *iodine and phosphorus*, it exhibits the usual reactions of alcohols. With *potassium* (or *sodium*) it yields a substitution-product. Heated with *quicklime*, it yields hydrogen and gaseous hydrocarbons. It reduces *oxide* (but not nitrate) of *silver*, when heated with it, forming a metallic mirror. (Bouis.)

**OCTYL, HYDRIDE OF.** $C^8H^{18} = C^8H^{17}.H$. *Hydride of Capryl.*—This hydrocarbon is one of the constituents of American petroleum, and is found in the portion of the oil boiling between 115° and 120° (Pelouze and Cahours, Ann. Ch. Pharm. cxxvii. 197; Jahresb. 1863, p. 528); also among the light oils obtained by distilling Wigan cannel-coal at a low temperature (Schorlemmer, Chem. Soc. J. xv. 419). It is produced, together with many of its homologues, by the action of zinc-chloride on amylic alcohol, passing over, together with octylene, in the portion of liquid which distils between 110° and 130°; and on treating this distillate with bromine which unites with the octylene, and distilling again under a pressure of 20 mm., the octylic hydride passes over at 80° (Wurtz, Ann. Ch. Pharm. cxxviii. 230; Jahresb. 1863, p. 509). It is a colourless liquid, having a faint ethereal odour, boiling at 119° (Schorlemmer), at 115°—118° (Wurtz), at 116°—118° (Pelouze and Cahours). Specific gravity = 0·728 at 0° (Wurtz). Vapour-density 4·01 (Wurts), calc. = 3·947. Chlorine converts it into chloride of octyl.

**OCTYL, IODIDE OF.** $C^8H^{17}I$. (Bouis, Ann. Ch. Phys. [3] xliv. 131. —Squire, Chem. Soc. Qu. J. vii. 108.)—Obtained by the action of iodine and phosphorus on octylic alcohol. It is an oily liquid, having an odour of oranges, boiling with decomposition at 211° (Bouis), at 193° (Squire). Specific gravity = 1·31 at 16° (Bouis). It burns with a smoky flame, and turns red on exposure to light. Heated with *alcoholic ammonia*, it yields hydriodate of octylamine (Squire, Cahours, Bouis); if the octylic iodide is in excess, di- and tri-octylamine are likewise formed

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* The analyses of castor-oil, alcohol, which agree more nearly with the 7-carbon formula, have been already given (iii. 146).

(Bouis). With *sodium* or potassium, it behaves like the chloride. Heated with *protosulphide of sodium* in alcoholic solution, it forms sulphide of octyl and iodide of sodium. Heated with *mercury*, it yields mercurous iodide, octylene, and free hydrogen. Its alcoholic solution precipitates *silver-salts*. (Bouis.)

**OCTYL, OXIDE OF.** $(C^8H^{17})^2O$ ?—Obtained, though not pure, by distilling octylate of sodium with chloride of octyl; also by distilling octylic alcohol with sulphuric acid, the acid being heated in a retort and the alcohol allowed to flow in slowly. (Bouis.)

**OCTYL, SULPHIDE OF.** $(C^8H^{17})^2S$.—When an alcoholic solution of protosulphide of sodium is heated with iodide of octyl, till the mixture becomes turbid, sulphide of octyl separates as an oily liquid, lighter than water, and having an unpleasant odour. It is slightly soluble in alcohol; decomposes when heated. (Bouis.)

**OCTYLAMINE.** *Caprylamine.* $C^8H^{19}N = C^8H^{17}.H^2.N$. (W. S. Squire, Chem. Soc. Qu. J. vii. 108.—Cahours, Ann. Ch. Pharm. xcii. 399.—Bouis, Ann. Ch. Phys. [3] xliv. 139.—Pelouze and Cahours, Jahresb. 1863, p. 529.)—A base produced by heating alcoholic ammonia with iodide of octyl (Squire, Cahours, Bouis), or with the chloride (Pelouze and Cahours); also by distilling a mixture of octylsulphate and cyanate of potassium, and treating the resulting distillate (which crystallises readily, and probably consists of cyanate and cyanurate of octyl) with potash. (Bouis.)

Octylamine is a colourless, bitter, very caustic, inflammable liquid, having an ammoniacal fishy odour. Specific gravity 0·786 (Squire). Boiling point 164° (Squire); 172°—175° (Cahours); 175° (Bouis); 168°—172° (Pelouze and Cahours). Octylamine is insoluble in water. It precipitates metallic salts, and dissolves chloride of silver. With *iodide of octyl*, it yields di- and tri-octylamine. With the *chlorides of benzoyl* and *cumyl*, it forms octyl-benzamide, and octyl-cumylamide. (Cahours.)

Octylamine unites readily with acids. The *hydriodate*, $C^8H^{20}NI$, forms large plates, easily soluble in water. The *hydrochlorate*, $C^8H^{20}Cl$, is very deliquescent, but ultimately crystallises in vacuo, in large nacreous plates. The *chloroaurate*, $C^8H^{20}NAuCl^4$, is deposited from dilute solutions in shining yellow laminæ resembling iodide of lead. The *chloroplatinate*, $C^8H^{20}NPtCl^3$, separates from boiling solutions in shining golden-yellow scales or large thin plates, easily soluble in alcohol and ether. The *nitrate*, $C^8H^{20}N.NO^3$, and *sulphate*, $(C^8H^{20}N)^2SO^4$, are crystallisable and readily soluble in water.

**OCTYLENE.** *Caprylene.* $C^8H^{16}$.—This hydrocarbon is produced, as already mentioned, by heating octylic alcohol with sulphuric acid or fused chloride of zinc (Bouis); by heating iodide or chloride of octyl with sodium or mercury (Bouis); by heating chloride of octyl with alcoholic potash (Pelouze and Cahours); also, together with several other olefines and many alcoholic hydrides, by the action of chloride of zinc on amylic alcohol (Wurtz). It is also formed together with hydrogen, marsh-gas, and other gaseous hydrocarbons, when pelargonic acid is distilled with potash-lime, constituting the greater part of the liquid distillate thus obtained, which passes over between 106° and 110° (Cahours, Compt. rend. xxxi. 143). It may be obtained in like manner from other fatty acids, viz. œnanthylic, caprylic, palmitic acid, &c., and appears to be produced in the distillation of most fixed oils.

Octylene is a very mobile oil, lighter than water and insoluble therein, very soluble in alcohol and ether. It boils without decomposition at 125° (Bouis); at 116°—120° (Cahours); at 118°—120° (Pelouze and Cahours); below 120° (Wurtz); at 115°—117° (Schorlemmer). Vapour-density, obs. = 3·86—3·90 (Bouis); 4·0 (Wurtz); 4·17 (Schorlemmer); calc. = 3·878. It burns with a very bright flame.

It is violently attacked by strong *nitric acid*, yielding nitro- and dinitro-octylene (Cahours). When treated first with sesqui-hydrated nitric acid, $2HNO^3.3H^2O$, and then with a mixture of fuming nitric acid and oil of vitriol, it yields dinitro-octylene, $C^8H^{14}(NO^2)^2$, which, after washing and drying, forms an oily liquid, heavier than water, and slightly soluble in water, forming a solution having a strongly irritating odour. It is decomposed by distillation, giving off red vapours, leaving a black residue, and yielding a distillate of nitro-octylene, $C^8H^{15}NO^2$, a liquid possessing similar properties. Octylene is not attacked by sodium, but if dry *chlorine gas* is passed into the liquid, a violet-coloured compound having the composition $C^8H^{15}ClNa^2$ or $C^8H^{16}Na.NaCl$, is formed, with evolution of hydrogen. With *iodine* and *bromine*, corresponding compounds are formed. (Bouis.)

**Meta-octylene,** $C^{16}H^{32}$ ?—A hydrocarbon polymeric with octylene, obtained by the prolonged action of fuming sulphuric acid on octylic alcohol. When purified by washing with water, alcohol and aqueous potash, it forms a colourless inodorous liquid of specific gravity 0·814 at 15°, and boiling with decomposition at 250°. It is insoluble in water, nearly insoluble in cold alcohol, burns with a bright flame, is not acted on by boiling potash. (Bonis.)

**OCTYLENE, ACETATE OF.** $C^{12}H^{22}O^4 = \left.\begin{matrix}(C^8H^{16})''\\(C^2H^3O)^2\end{matrix}\right\}O^2$.—Obtained by heating an ethereal solution of the bromide with acetate of silver to 100°. It is a thick oily liquid, boiling between 240° and 245° (Wurtz); 245° and 250° (De Clermont).

**OCTYLENE, BROMIDE OF.** $C^8H^{16}Br^2$.—Produced by direct combination (*e.g.* by the action of bromine on the mixture of octylene and octylic hydride occurring amongst the products of the decomposition of amylic alcohol by chloride of zinc). It is an amber-coloured heavy liquid, which cannot be distilled without decomposition, even in rarefied air. (Wurtz.)

**OCTYLENE, HYDRATE OF.** $C^8H^{18}O^2 = (C^8H^{16})''.H^2.O^2$. *Octylic Glycol. Octylenic alcohol.* (P. De Clermont, Compt. rend. lix. 80; Ann. Ch. Pharm. Suppl. iii. 254.)—Obtained by decomposing the acetate with finely pulverised potash added by small portions, distilling in an oil-bath, repeating the whole process several times, and purifying the product by fractional distillation. It is a thick, oily, colourless, inodorous liquid, having a burning aromatic taste, insoluble in water, soluble in alcohol and in ether. Specific gravity = 0·932 at 0°, and 0·920 at 29°. Boils between 235° and 240°.

**OCTYLENE, HYDRATOCHLORIDE OF.** $C^8H^{17}ClO = \left.\begin{matrix}(C^8H^{16})''Cl\\HO\end{matrix}\right\}$ *Octylenic Chlorhydrin.*—This compound is formed: 1. By the action of strong hydrochloric acid on octylenic alcohol;—2. By the action of hypochlorous acid on octylene. The first reaction yields a very impure product. To prepare the compound by the second, pure octylene is added to a solution containing 2 or 3 per cent. hypochlorous acid, obtained, according to the method of Carius (Ann. Ch. Pharm. cxxvi. 195), by agitating chlorine gas as free as possible from air, with mercuric oxide previously heated to 300°, and suspended in a small quantity of water.*

The product is a mixture of mercuric oxychloride, water, and hydratochloride of octylene. The latter is extracted by ether, the mercury precipitated by sulphydric acid, the excess of acid neutralised by carbonate of sodium, and the liquid submitted to fractional distillation. The hydratochloride is then obtained nearly pure, in the form of an aromatic liquid boiling between 204° and 208°. (De Clermont, *loc. cit.*)

**OCUBA-WAX.** A vegetable wax obtained from the fruit of *Myristica ocuba, officinalis* or *sebifera*, a plant growing abundantly in the marshy grounds on the shores of the Amazon and its tributaries. The shelled fruit, bruised and boiled with water, yields from 18 to 19 per cent. of the wax, which is yellowish-white, of the consistence of bees-wax, melts at 36°, dissolves in boiling alcohol. It contains, according to Lewy's analysis, 74·0 per cent. carbon, 11·3 hydrogen, and 14·7 oxygen, but is most probably a mixture of different fats. It is easily bleached, and is used extensively in Brazil for the manufacture of candles.

**ODMYL.** (Anderson, Ann. Ch. Pharm. lxiii. 370.)—When fats or oils containing oleic acid are distilled with sulphur, a fetid oil passes over, which may be separated by rectification into several others, the first of which is a limpid oil boiling at about 71°; but the quantity of this limpid oil is but small, and it is not found possible to obtain fractions of constant boiling point. The crude oil dissolved in alcohol yields precipitates with various metallic salts. With mercuric chloride, a white precipitate is formed, yielding by analysis, 14·61 per cent. carbon, 2·72 hydrogen, 60·01 mercury, 10·25—10·67 chlorine, and 12·48 sulphur, whence Anderson deduces the formula $C^8H^8S^2.2HgCl + C^8H^8S^2.Hg^2S$, regarding the precipitate as a compound of mercuric chloride and mercurous sulphide with the body $C^8H^8S^2$, which he calls *sulphide of odmyl*. Gerhardt, on the other hand (*Traité*, ii. 637), suggests the formula $C^4H^9HgS.HgCl$. (requiring 14·76 C, 2·80 H, 61·22 Hg, 11·07 Cl and 10·15 S), representing it as a compound of mercuric chloride with mercuric sulphotetrylate (analogous to mercuric sulphethylate or mercaptide, ii. 548). The mercury precipitate suspended in water is blackened and decomposed by sulphydric acid, and the liquid yields by distillation a limpid oil, lighter than water, and having a repulsive odour like that of certain umbelliferous plants. This oil (regarded by Anderson as *sulphide of odmyl*, but perhaps consisting of tetryl-sulphydric acid, or tetrylic mercaptan) gives with alcoholic mercuric chloride a white precipitate, exactly resembling the preceding, and with platinic chloride a yellow precipitate similar to that obtained with the limpid oil obtained by rectifying the crude sulphuretted oil.

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* The proportions required are 15 grms. mercuric oxide to a litre of chlorine. The agitation must be performed in a dark place and in bottles not containing more than a litre. With larger quantities, the process fails from formation of mercuric chlorate. Pure hypochlorous acid is not well adapted for experiments like the above, as it easily gives off chlorine, even in dilute solution. The solution obtained as just described should therefore be mixed with a small additional quantity of mercuric oxide previously heated to 300° and suspended in a small quantity of water. (Carius.)

**ODORINE.** A volatile base obtained by Unverdorben from bone-oil. It appears to have been impure picoline.

**ODONTOLITE.** See TURQUOIS.

**ŒNANTHIC ACID** and **ETHER.** (Liebig and Pelouze, Ann. Ch. Pharm. xix. 241.—Delffs, *ibid.* lxxx. 290).—The name œnanthic ether was given by Liebig and Pelouze to an ethereal liquid which exists in all wines and is the source of their peculiar odour, causing a few drops of wine left in a bottle to be distinctly smelt, whereas a mixture of pure alcohol and water of the same alcoholic strength as wine has scarcely any odour. This ether remains in small quantity as an oily liquid,[*] when large quantities of wine are distilled; it may be obtained with greater facility by distilling wine-lees with half its bulk of water, taking care that the mass does not carbonise. The distillate contains a small quantity of free acid from which it may be freed by washing with aqueous carbonate of sodium.

When thus purified and dried, œnanthic ether is a very mobile liquid, having a very strong vinous odour, almost intoxicating when inhaled. Its taste is very strong and disagreeable. It dissolves easily in ether and in alcohol, even when the latter is rather dilute, not perceptibly in water. Sp. gr. = 0·862 (Liebig and Pelouze); 0·8725 at 15·5° (Delffs). Boils between 225° and 230° (L. and P.); at 224° (Delffs). It gives by analysis 70·5—71·5 per cent. carbon and 11·8—12·1 hydrogen, whence Liebig and Pelouze deduce the formula $C^{18}H^{18}O^{3}$ (calc. 72·0 per cent. C and 12·0 H), regarding the compound as the ethylic ether of œnanthic acid, $C^{14}H^{14}O^{3}$. Delffs, on the other hand, considers it to be identical with pelargonate of ethyl, $C^{22}H^{22}O^{4}$ or $C^{11}H^{22}O^{2}$ = $C^{9}H^{17}(C^{2}H^{5})O^{2}$, (requiring 71·0 per cent. C and 11·8 H). The vapour-density is 9·8 according to Liebig and Pelouze; 7·04 at 270° according to Delffs; the calculated vapour-density of pelargonic ether is 6·45.

By treating œnanthic ether with an alkali, and decomposing the product with sulphuric acid, œnanthic acid is obtained as an oil which may be washed with warm water, and dried with chloride of calcium, or in vacuo over oil of vitriol. This acid forms at 13° a colourless buttery mass, melting at a higher temperature to a colourless, tasteless, inodorous oil, which reddens litmus, and dissolves easily in alkalis and alkaline carbonates, also in ether and in alcohol. It contains, according to Liebig and Pelouze, 68·6—67·5 per cent. carbon, and 11·6 hydrogen, whence they deduce the formula $C^{14}H^{14}O^{3}$ (calc. 68·85 C, and 11·5 H). Delffs, on the other hand, regards it as pelargonic acid, $C^{18}H^{18}O^{4}$ or $C^{9}H^{18}O^{2}$, which requires 68·35 C and 11·40 H. The silver-salt gives by analysis 35·7 per cent. silver (L. and P.); 27·1 (Mulder); 40·5 (Delffs); pelargonate of silver contains 40·75 per cent.

Œnanthic acid, when distilled, first gives off a mixture of water and the unaltered acid, afterwards the so-called *anhydrous œnanthic acid*, $C^{14}H^{13}O^{2}$, in the form of a liquid, which begins to boil at 260°, solidifies at 31°, and contains, according to Liebig and Pelouze, 73·3—74·3 C, and 12·2 H. Now, as pelargonic acid when heated distils altogether unaltered, Liebig still regards œnanthic acid as distinct from pelargonic acid. The point, however, requires further investigation, as it is evident that neither the acid nor the ether has been obtained pure. According to Fischer (Ann. Ch. Pharm. cxv. 247), the so-called œnanthic acid is a mixture of capric and caprylic acids.

**Chlorœnanthic Acid** and **Ether.** Malaguti (Ann. Ch. Phys. [2] lxx. 363), by treating œnanthic ether with chlorine, obtained a bitter, fragrant, syrupy liquid, sparingly soluble in alcohol, having a specific gravity of 1·2912 at 16°, decomposed by distillation, and containing 37·15 per cent. C, 5·30 H, and 48·55 Cl, whence he deduces the formula $C^{18}H^{14}Cl^{4}O^{3}$. When decomposed by potash, it yields an oily acid containing 43·2—43·4 per cent. C, 6·3—6·6 H, and 36·0—36·3 Cl, agreeing approximately with the formula $C^{14}H^{12}Cl^{2}O^{3}$.

For further details respecting all these compounds, see *Gmelin's Handbook*, xii. 455—460.

**ŒNANTHOL.** $C^{7}H^{14}O = C^{7}H^{13}O.H$. *Hydride of Œnanthyl. Œnanthylic Aldehyde.* (Bussy and Lecanu, J. Pharm. xiii. 62.—Bussy, *ibid.* [3] 8, 321. —A. W. Williamson, Ann. Ch. Pharm. lxi. 38.—Tilley, Phil. Mag. xxxiii. 81.—Bertagnini, Ann. Ch. Pharm. lxxxv. 281.—Bouis, Ann. Ch. Phys. xliv. 87.)—This body, which is the aldehyde of œnanthylic acid, and isomeric with butyrone, is produced by the dry distillation of castor-oil; also, according to Petersen (Ann. Ch. Pharm. lxxxv. 281), together with propylic aldehyde and other products, by the dry distillation of sebate of calcium.

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[*] A *solid* substance called œnanthic ether, which is manufactured in Bavaria, and used for flavouring inferior wines, was exhibited by M. Lichtenberger in the International Exhibition of 1862. (*Hofmann's Report*, p. 113.)

*Preparation.*—1. The yellow oily distillate obtained by the dry distillation of castor-oil is separated from the watery liquid and distilled with five or six times its bulk of water; the distillate consisting of œnanthol, with small quantities of acrolein, œnanthylic acid and oily fatty acids, is shaken up with 6 pts. by weight of water, which dissolves out the greater part of the acrolein, and again distilled with pure water, till no more oily liquid remains; this distillate is shaken up with weak baryta-water till it no longer exhibits an acid reaction, then decanted and distilled; and the portion which goes over between 155° and 158°, is collected apart (below 150°, acrolein distils over). The pure œnanthol thus obtained is dehydrated by chloride of calcium (Bussy, Williamson).—2. The product of the dry distillation of castor-oil is shaken up with a solution of carbonate of potassium, whereby a solution is formed which when heated to the boiling point yields the œnanthol as a separate layer on the surface; this liquid is removed, and treated with a moderately concentrated solution of acid sulphite of sodium, which dissolves the œnanthol, and leaves an oily liquid smelling like a fixed oil. The solution on cooling deposits sulphite of œnanthol and sodium, which must be dried and decomposed with warm water containing hydrochloric or sulphuric acid (Bertagnini). See also Delffs (Jahresb. 1860, p. 320).

*Properties.*—Œnanthol is a transparent, colourless, very mobile liquid, of sp. gr. 0·827. It has a strong, not unpleasant odour, and a taste sweet at first, but afterwards persistently sharp. Refracts light strongly. Boils between 155° and 158° (Bussy); 155° and 156° (Williamson); at 155° (Tilley); between 151° and 152° (Städeler, Jahresb. 1857, p. 360). Vapour-density = 4·139 (Bussy); from 4·08 to 5·01 (Bouis): by calculation 3·952.

It dissolves very sparingly in *water*, imparting its odour, and mixes in all proportions with *alcohol* and *ether*.

When moist œnanthol is exposed for some time to a low temperature, it yields colourless crystals of a hydrate $2C^7H^{14}O.H^2O$, smelling like œnanthol itself. (Bussy.)

*Decompositions.*—1. When œnanthol is subjected to continued distillation, the boiling point rises, and the residue in the retort exhibits a greater amount of carbon (Tilley, Bouis).—2. In contact with the air, it absorbs oxygen and turns sour; when shaken up with *oxygen*, it may absorb as much as 10 per cent.; at the boiling point the absorption goes on faster (Bussy).—When œnanthol which is kept cool, is gradually mixed with a quantity of *bromine*, sufficient to render the brown-red colour permanent, and repeatedly distilled with water, a colourless liquid is obtained, which turns brown when dried by chloride of calcium, or over oil of vitriol, and after being freed from dissolved hydrobromic acid by caustic soda, contains 40·90 per cent. C, 6·53 H, and from 44·6 to 45·7 Br ($C^7H^{13}BrO$ requires 43·5 per cent. C, 6·7 H, and 41·4 Br). On distilling it with water a brown resin remains in the retort. When œnanthol is mixed with *iodine* and *phosphorus*, a violent explosion ensues (Limpricht).—4. Œnanthol is converted by cold *nitric acid* of ordinary strength into metœnanthol; when distilled with 2 pts. of a mixture of 1 vol. strong nitric acid and 1 vol. water, it is gradually converted into œnanthylic acid (Bussy). When œnanthol is heated with 2 pts. of strong nitric acid, great heat is produced, red vapours are given off, and the greater part of the œnanthol is destroyed (Bussy). When œnanthol is added by drops to strong nitric acid contained in a retort, a violent action takes place, and a mixture of nitracrol (p. 58), œnanthylic acid, caproic acid and nitric acid distils over, the liquid in the retort containing œnanthylic and caproic acids (Tilley).—5. With *chlorine*, œnanthol forms hydrochloric acid and chlorœnanthol (Williamson).—6. Œnanthol dropped upon crystallised *chromic acid* takes fire with violent explosion; dilute chromic acid converts it into œnanthylic acid (Bussy).—7. With fuming *oil of vitriol*, it forms a conjugated acid, which yields crystallisable salts with baryta, lime, and oxide of lead (Bouis).—8. When repeatedly distilled over *phosphoric anhydride*, it yields œnanthylene (Bouis).—9. With *pentachloride of phosphorus*, it becomes strongly heated, and yields a distillate, which when freed from oxychloride of phosphorus by repeated washing with water, and from excess of œnanthol by agitation with acid sulphite of sodium, consists of nearly pure chloride of heptyl (Limpricht).—10. Œnanthol dropped upon fused *hydrate of potassium* gives off hydrogen, and forms œnanthylate of potassium (Tilley).

$$C^7H^{14}O + KHO = C^7H^{13}KO^2 + H^2.$$

When it is mixed with a strong aqueous solution of potash, considerable rise of temperature takes place, and a salt of œnanthylic acid is produced, together with an oil, which is decomposed by simple distillation, and after being washed or distilled with water, contains 76·4 per cent. C and 12·4 per cent. H, and is therefore not œnanthol. Heated with alcoholic potash, œnanthol yields œnanthylic acid, and an oil which when dried by chloride of calcium, contains 77·1 per cent. C and 12·7 H. (Williamson.)

11. Distilled with *quicklime*, it yields a distillate containing heptylene, octylene, nonylene, and hydrocarbon of still higher boiling point, also heptylic alcohol and œnanthyl-acetone, or hexyl-œnanthyl, $C^{13}H^{26}O$. (Fittig, Ann. Ch. Pharm. cxxii. 76.)

12. An alcoholic solution of œnanthol, through which *hydrochloric acid gas* is passed, yields œnanthylate of ethyl (Tilley).—13. Œnanthol reduces *nitrate of silver;* when it is mixed with ammonia and nitrate of silver added, a white precipitate is formed, which is reduced by heating, and silvers the vessel. (Bussy.)

14. Œnanthol, gently heated with *zinc-ethyl*, forms a compound containing $C^{14}H^{26}O$, together with hydride of ethyl and hydrate of zinc:

$$4C^7H^{14}O + Zn(C^2H^5)^2 = 2C^{14}H^{26}O + 2C^2H^6 + ZnH^2O^2.$$

The compound $C^{14}H^{26}O$ is not of constant boiling point. (Rieth and Beilstein, Ann. Ch. Pharm. cxxvi. 241.)

*Combinations.* α. With Ammonia.—Œnanthol absorbs a large quantity of ammonia gas, forming at first a crystalline compound, which afterwards liquefies and is completely decomposed by water (Tilley, Limpricht.)—This ammoniacal compound, gently heated with hydrocyanic and hydrochloric acids (as in the preparation of alanine from valeraldehyde, i. 63) yields a yellowish amorphous body, which crystallises from strong hydrochloric acid in needles, and appears to have the composition $C^8H^{17}NO^2.HCl$. (Erlenmeyer and Schäffer, Jahresh. 1863, p. 366.)

β. With Acid Sulphites of Alkali-metals.—Œnanthol unites directly with these salts, forming more or less crystalline compounds, which may likewise be obtained by passing sulphurous anhydride into a recently prepared solution of œnanthol in alcoholic ammonia, potash or soda.

The *ammonium-salt*, $C^7H^{15}(NH^4)SO^4$, forms small shining prisms, sparingly soluble in water and in alcohol. They are decomposed by boiling with water, giving off œnanthol, and leaving a solution of acid sulphite of ammonium. Heated with potash-lime, or by itself in a sealed tube to 260°—270°, it yields tri-hexylamine, $C^{18}H^{39}N = N(C^6H^{13})^3$. (Petersen and Gössmann, Jahresb. 1857, p. 388.)

The *potassium-salt* is obtained as a pulpy mass, which gradually becomes crystalline, and separates from alcoholic solution in small needles.

The *sodium-salt*, $C^7H^{15}NaSO^4.2H^2O$, crystallises in very brilliant interlaced scales, unctuous to the touch, and exhaling the odour of œnanthol. They dissolve easily in water, either cold or warm, without decomposition, but the solution is decomposed by boiling, especially in presence of an acid or an alkali, drops of œnanthol separating out. The crystals dissolve very easily in hot alcohol, but are nearly insoluble in cold alcohol.

The aqueous solution forms with salts of *barium*, *lead*, or *silver*, copious precipitates containing œnanthol chemically combined.—*Ammonia* added to the aqueous solution forms an abundant curdy precipitate, which soon disappears, oily drops collecting at the same time on the surface of the liquid.—The cold aqueous solution is not decomposed by addition of a large quantity of *sulphuric* or *hydrochloric acid*, the compound even crystallising unaltered from an acid solution. *Chlorine* and *bromine* decompose it instantly at ordinary temperatures; iodine only with aid of heat.

TRICHLORŒNANTHOL, $C^7H^{11}Cl^3O$.—Produced by the action of chlorine gas on œnanthol. It is a viscid oil heavier than water, and having an agreeable odour somewhat like that of caoutchouc. It blackens when distilled, giving off hydrochloric acid.

**Metœnanthol,** $C^7H^{14}O$.—This compound, isomeric with œnanthol, is produced by agitating the latter with nitric acid at 0°. If the liquid be then left to itself for 24 hours, then poured into a shallow dish, and exposed in a cold place, metœnanthol is obtained in beautiful crystals, which remain solid up to the temperature of 5° or 6°, are inodorous, dissolve in boiling alcohol, and finally crystallise again on cooling. The compound melts when heated, and boils at 230°. It is not decomposed at ordinary temperatures by ammonia, potash or soda. (Bussy.)

**ŒNANTHYL.** $C^7H^{13}O$.—The hypothetical radicle of œnanthylic acid and its derivatives. The same name is sometimes, but inappropriately, given to heptyl, $C^7H^{15}$.

**ŒNANTHYL, CHLORIDE OF.** $C^7H^{13}OCl$.—Obtained by distilling œnanthylic acid with pentachloride of phosphorus. It is decomposed by water into hydrochloric and œnanthylic acids. (Cahours, Compt. rend. xxv. 724.)

**ŒNANTHYL, HYDRIDE OF.** Syn. with ŒNANTHOL (p. 174.)

**ŒNANHTYL-ACETONE.** See Œnanthylone (p. 178)

**ŒNANTHYLAMIDE.** $C^7H^{15}NO = N.H^2.C^7H^{13}O$. *Azoture d'œnanthyle.*—Produced by the action of ammonia on œnanthylic anhydride. Crystallises from a boiling dilute alcoholic solution in small scales; occasionally, however, the crystallisation does not begin till some time after the solution has completely cooled. (Chiozza and Malerla, *Gerhardt's Traité*, ii. 728.)

**ŒNANTHYLENE.** Syn. with Heptylene (iii. 14).

**ŒNANTHYLIC ACID.** $C^7H^{14}O^2 = \left.\begin{matrix}C^7H^{13}O\\H\end{matrix}\right\}O$. (Laurent, Ann. Ch. Phys. lxvi. 173.—Tilley, Ann. Ch. Pharm. xxxix. 160; lxvii. 106.—Bussy, J. Pharm. [3] viii. 329.—Schneider, Ann. Ch. Pharm. lxx. 112.—Arzbächer, *ibid.* cxxiii. 200.—Brazier and Gossleth, *ibid.* lxxvi. 268).—This acid was first obtained by Laurent in an impure state, and called *azoleic acid;* Berzelius called it *aboleic acid.* It occurs in the fusel-oil of spirit prepared from maize.

It is produced by the oxidation of œnanthol in the air, or in oxygen gas, or when that compound is boiled with nitric acid (Bussy, Tilley), or with chromic acid (Brazier and Gossleth); also by boiling castor-oil with dilute nitric acid (Tilley), or with chromic acid (Arzächer); by heating the distillate obtained from castor-oil with nitric acid (Schneider, Ann. Ch. Pharm. lxx. 112), or that from oleic acid with strong nitric acid (Laurent, Redtenbacher, lix. 41); by oxidising heptylic alcohol with chromate of potassium and sulphuric acid (Schorlemmer, Proc. Roy. Soc. xiv. 171); by the action of nitric acid on Chinese wax, (Buckton, Chem. Soc. J. x. 166); on azelaic acid, and on spermaceti (Arppe, Ann. Ch. Pharm. cxx. 288); by the action of potash on œnanthol (Bussy, p. 175); and by melting sebacic acid with potash (Koch. Ann. Ch. Pharm. cxix. 173).

*Preparation.*—1 pt. of œnanthol is distilled with 2 pts. of a mixture of 1 vol. strong nitric acid and 2 vol. water till the greater part has passed over; the oily distillate decanted from the acid water, is saturated with baryta-water and evaporated to the crystallising point; and the barium-salt which crystallises out is decomposed by sulphuric or phosphoric acid; the œnanthylic acid then rises to the surface in the form of a colourless liquid. An additional quantity of œnanthylate of barium may be obtained by washing the residue in the retort with water, which extracts oxalic and nitric acids, and neutralising with baryta-water. (Bussy.)

2. A mixture of 1 pt. castor-oil and 2 pts. of nitric acid, diluted with an equal bulk of water, is heated in a retort; a violent action then takes place, so that the retort must be removed from the fire till it diminishes, after which the distillation is continued for several days. The receiver contains the oily acid; the retort, the watery liquid and a thick fatty substance which, when distilled with water, yields a large additional quantity of the oily acid. The product is washed with water, distilled with water, and dried by fused phosphoric acid. (Tilley.)

*Properties.*—Œnanthylic acid is a transparent colourless oil, having an unpleasant odour like that of cod-fish, faint in the cold, but becoming stronger at higher temperatures, and a pungent exciting taste. It begins to boil at 148°, but decomposes and blackens when subjected to continued distillation (Tilley); boils at 212° (Strecker), Lehrb. v. 96). According to Städeler (Jahresb. 1857, p. 148), it has a specific gravity of 0·9167 at 24°, and boils at 218° It dissolves in strong *nitric acid*, and is precipitated therefrom by water. It is soluble in *alcohol* and in *ether.*

*Decompositions.*—1. Œnanthylic acid burns with a white flame (Tilley).—2. Heated with *soda-ley* it forms a neutral oil (Arzbächer).—3. Heated with *potash-lime* it yields gaseous and liquid hydrocarbons of the formula $C^nH^{2n}$ (Cahours, Compt. rend. xxxi. 141).—4. Heated with *baryta*, it yields a hydrocarbon, boiling at about 58°, and having the composition of hydride of hexyl, $C^6H^{14}$ (Riche, Jahresb. 1860. p. 249).—5. When distilled with *pentachloride of phosphorus*, it yields chloride of œnanthyl (Cahours, Compt. rend. xxv. 724).—6. A concentrated solution of œnanthylate of potassium decomposed by a current of six Bunsen's cells, gives off hydrogen and carbonic acid, while neutral acid and carbonate of potassium are formed, and an oil rises to the surface, which when distilled with potash, leaves œnanthylate of potassium and yields a distillate, consisting mainly of hexyl and a hydrocarbon, $C^{12}H^{26}$, boiling at 170°. (Brazier and Gossleth.)

Œnanthylates. $C^7H^{13}MO$ and $C^{14}H^{26}M''O^4$.—The *ammonium* and *potassium salts* are very soluble in water.—The *barium-salt*, $C^{14}H^{26}Ba''O^4$ (prepared as above) forms white nacreous scales or lancet-shaped tablets. It has a faint, slightly bitter taste, exhales an odour of perspiration when rubbed between the fingers; dissolves in 67 pts. water, at 23° (Bussy), very easily in hot water, still more easily in hot alcohol of 85 per cent. (Arzbächer); insoluble in ether.—The *copper-salt* separates after a while from a mixture of the free acid with cupric acetate, in needles having a fine green colour and silky lustre.—The *lead-salt* is precipitated by neutral acetate of lead, from a solution of œnanthylate of potassium, as a lemon-yellow powder, insoluble in water, but soluble in boiling alcohol, whence it separates in small scales on cooling.—The *silver-salt*, $C^7H^{13}AgO^2$, is obtained on adding nitrate of silver to the acid neutralised with ammonia, as a white precipitate, insoluble in water, and turning brown on exposure to light. By dry distillation, it yields an oil, and a solid substance which crystallises in needles from hot alcohol; both are acid.

**ŒNANTHYLIC ANHYDRIDE.** $C^{14}H^{26}O^3 = \left.\begin{matrix}C^7H^{13}O\\C^7H^{13}O\end{matrix}\right\}O$.—*Œnanthylate of Œnanthyl. Anhydrous-Œnanthylic acid.* (Chiozza and Malerba, Ann. Ch. Pharm. xci. 102).—Produced by the action of pentachloride of phosphorus on œnanthylate of potassium. It is a colourless oil, of specific gravity 0·91 at 14°. At ordinary temperatures it has a faint odour, like that of caprylic anhydride. It gives out an aromatic odour when heated, and smells rancid if kept in badly closed vessels.

With alkalis it behaves like other anhydrides, and with caustic ammonia it yields œnanthylamide, $N.C^7H^{13}O.H^2$.

**ŒNANTHYLIC ETHERS.** 1. *Œnanthylate of Ethyl*, $C^7H^{13}(C^2H^5)O^2$, is obtained by passing hydrochloric acid gas through an alcoholic solution of œnanthylic acid (Tilley), or œnanthol (Williamson). It is a colourless oil, lighter than water, and solidifying in a freezing mixture; has a pleasant fruity odour; is insoluble in water but dissolves easily in alcohol and ether; distils easily but with constantly rising boiling'point; burns with a clear but fuliginous flame.

2. *Œnanthylate of Phenyl*, $C^7H^{13}(C^6H^5)O^2$, produced by the action of chloride of œnanthyl on phenylic alcohol, is an oil boiling between 275° and 280°. (Cahours, Compt. rend. xxxviii. 257.)

**ŒNANTHYLO-BENZOIC ANHYDRIDE.** $C^7H^{13}O.C^7H^5O.O$.—See BENZO-ŒNANTHYLIC ANHYDRIDE (i. 558).

**ŒNANTHYLO-CUMINIC ANHYDRIDE.** $C^7H^{13}O.C^{10}H^{11}O.O$.—See CUMIN-ŒNANTHYLIC ANHYDRIDE (ii. 180).

**ŒNANTHYLONE.** $C^{13}H^{26}O = C^7H^{13}O.C^6H^{13}$. *Œnanthyl-acetone.* (Uslar and Seekamp, Ann. Ch. Pharm. cviii. 179.)—Produced by the dry distillation of œnanthylate of calcium, and purified by rectification and crystallisation from alcohol. It crystallises in large colourless laminæ, of specific gravity 0·825, melts at 30°, solidifies again at 29·5°, boils at 264°.

Tilley (Ann. Ch. Pharm. lxvii. 110), by heating 1 pt. of œnanthol with 5 or 6 pts. hydrate of potassium, obtained an oil boiling at 120°, and containing 79·3 per cent. carbon and 13·3 per cent. hydrogen. To this compound Tilley assigned the formula $C^{14}H^{14}O$ (requiring 78·2 per cent. C, 13·3 H, and 7·5 oxygen), designating it as *hydride of œnanthyl*. Gmelin (*Handbook*, xii. 451) suggests that it may be œnanthylone, the formula of which requires 78·8 per cent. C, 13·1 H, and 8·1 O.

**ŒNANTHYL-SULPHURIC ACID.** Syn. with HEPTYL-SULPHURIC ACID (iii. 149).

**ŒNANTHYLOUS ACID.** Syn. with ŒNANTHIC ACID (p. 174).

**ŒNOL.** Syn. with MESITYLENE (Berzelius).

**ŒNOLIN.** $C^{10}H^{10}$ —A colouring matter obtained from red wine by precipitating with basic acetate of lead, exhausting the dried precipitate with ether containing hydrochloric acid, then with pure ether, digesting the air-dried residue with alcohol, and mixing the concentrated alcoholic solution with water. Œnolin is then precipitated in a mass, which is brown-red while moist, nearly black when dry, but yields a violet-red or brown-red powder; it is nearly insoluble in pure water, more soluble in water containing vegetable acids, easily soluble in alcohol, insoluble in ether. It forms a lead-compound containing $C^{30}H^{16}Ppb''O^{10}$. (Glénard, Compt. rend. xlvii. 268; Jahresh. 1851, p. 476.)

**ŒNOMETER.** A hydrometer specially adapted for determining the alcoholic strength of wines.

**ŒNYL.** Syn. with MESITYL.

**ŒRSTEDTITE.** A silico-titanate of zirconium occurring at Arendal in Norway, commonly in crystals of pyroxene, in dimetric crystals in which P : P = 123° 16'. Hardness = 5·5. Specific gravity = 3·629. It is opaque or subtranslucent, with reddish-brown colour, and splendent adamantine lustre. Infusible before the blowpipe, and according to Berzelius, gives a trace of tin. Contains, according to Forchhammer (Pogg. Ann. xxxv. 680), 19·71 per cent. silica, 68·79 titanic anhydride and zirconia, 2·61 lime, 2·05 magnesia, 1·14 ferrous oxide, and 5·52 water (= 100).

**OFFA HELMONTII.** An old name for acid carbonate of ammonium precipitated by alcohol from aqueous solution.

**OGKOITE.** See RIPIDOLITE.

**OIL GAS.** When a fat oil is made to fall in drops on iron or earthenware at a low red heat, it is for the most part resolved into a gaseous mixture of ethylene, marsh-gas, hydrogen, carbonic oxide, and the vapours of benzene and certain empyreumatic oils. The gas thus obtained is far superior in illuminating power to coal-gas, and was manufactured some years ago on a somewhat considerable scale, and sold, condensed in strong iron cylinders, as "portable gas;" but the process was not found profitable, and has been long since abandoned. For a description of it see *Ure's Dictionary of Chemistry*, 4th ed. p. 642.

**OIL, GENESSEE,** or **SENECA.** A name sometimes applied to American petroleum, because it was formerly collected and sold by the Seneca and other Indians.

**OIL, MINERAL.** See PETROLEUM.

**OIL OF VITRIOL.** Strong sulphuric acid.

**OIL OF WINE.** See ETHERIN (ii. 507).

**OILS.** The term "oil' was originally applied to certain well-known neutral compounds occurring in the bodies of living plants and animals, and possessing the following properties:—They are liquid at common temperatures; have a more or less viscid consistence; are insoluble or nearly insoluble in water, but dissolve more or less readily in alcohol, very easily and in all proportions in ether; take fire when strongly heated in the air, and burn either alone or by means of a wick, with a more or less fuliginous flame. There are many other liquids possessing the peculiar consistence called "oily," namely, some members of the fatty acid series, butyric, valerianic, caproic acid, &c., many organic bases, as the higher homologues of ethylamine, certain natural alkaloïds—nicotine and conine for example—and most of the compound ethers. But when we speak of an "oil" we generally mean a neutral body, formed by natural processes in the living animal or vegetable organism, and possessing the properties just specified; and in that sense the word will be used in the present article.

Natural Oils are divided into two great classes, fat or fixed oils, and volatile or essential oils.

### A.—FAT OR FIXED OILS.

These bodies exhibit very great similarity of chemical composition, most of them being glycerides, and resolvable by saponification into glycerin and certain fatty acids, chiefly stearic, palmitic and oleic acids. They further resemble one another in not being volatile, and not capable of distilling without decomposition, by which characters, as well as by their composition, they are easily distinguished from the volatile oils. Fat oils are divided into drying and non-drying oils. The former thicken when exposed to the air, absorbing oxygen, and being ultimately converted, if spread over a large surface, into a yellowish, transparent, supple membrane or varnish. This property renders them available for the preparation of varnishes and oil-colours. To this class belong linseed, nut, hemp and poppy oils; they contain an olein different from that of the non-drying oils, and yielding by saponification, not oleic, but linoleic acid or an acid similar thereto.

The non-drying oils are likewise gradually altered by exposure to the air, though in a different manner. They turn rancid, that is to say, they acquire an acrid, disagreeable taste, gradually lose their colour, and to a certain extent their fluidity, and acquire the power of reddening litmus. This alteration—which never takes place in pure glycerides, such as stearin, palmitin or olein, or in mixtures of them—is due to the presence of foreign matters, namely, the cellular substance of the plant or animal from which the oil has been extracted. These substances act as ferments, and give rise to the decomposition of a small quantity of fatty matter in contact with them, the palmitic, oleic acid, &c., of this portion of the oil being then set free, and small quantities of odorous volatile acids (butyric, valerianic caproic) being formed at the same time, probably from atmospheric oxidation. By exhausting rancid oils with boiling water, and treating them in the cold with a weak alkaline solution, they may be freed from these products of decomposition and restored to their original state.

The mode of occurrence of fat oils in the bodies of plants and animals, their decomposition by distillation, and their reactions with alkalis, acids, &c., have already been described under FATS and GLYCERIDES. The individual oils are described in their respective alphabetical places. For the methods of extraction on the large scale, and

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purification, see *Ure's Dict. of Arts,* &c. iii. 276. The following table exhibits a list of the principal vegetable fat oils, together with their specific gravities and solidifying points, so far as they have been determined. The specific gravities marked with an asterisk are, according to determinations (taken at 15°) by Cloez (Bull. Soc. Chim. 1865, p. 46): the rest, and the solidifying points, are taken from *Gmelin's Handbook.* The numbers in the last column denote the temperatures at which the oils become perfectly solid: nearly all of them, however, become viscous or semi-solid at temperatures somewhat higher.

| Name of Oil. | Name of plant which yields it. | Specific gravity. | Solidifying point. |
|---|---|---|---|
| 1. DRYING OILS. | | | |
| Cress-seed oil | *Lepidium sativum* | 0·924 | − 15° |
| Oil of Deadly Nightshade | *Atropa Belladonna* | 0·925 | − 27·5° |
| Oil of Gold-of-Pleasure seed | *Camelina sativa* | 0·93075* | − 19° |
| Gourd-seed oil | *Cucurbita Pepo* | 0·9231 | − 15° |
| Grape-seed oil | *Vitis vinifera* | 0·9202 | − 11° |
| Hemp-seed oil | *Cannabis sativa* | 0·93075* | − 27·5° |
| Oil of Honesty | *Hesperis matronalis* | 0·9232 | below − 15° |
| Linseed oil | *Linum usitatissimum* | 0·93515* | below − 20° |
| Oil of Madi | *Madia sativa* | 0·9286 at 15° | below − 10° |
| Poppy oil | *Papaver somniferum* | 0·92702* | − 18° |
| Sunflower oil | *Helianthus annuus* | 0·92504* | − 16° |
| Oil of Scotch Fir seed | *Pinus sylvestris* | 0·9312 | − 30° |
| Oil of Silver Fir cones | *Abies Picea*. Dec. | 0·926 | |
| Oil of Spruce Fir | *Abies excelsa*. Dec. | 0·9283 | below − 15° |
| Fatty oil of Spruce Fir | . . . . . . . | 0·904 | |
| Tobacco-seed oil | *Nicotiana Tabacum* | 0·9232 | − 15° |
| Walnut or Nut oil | *Juglans regia* | 0·92878* | − 18° |
| Weld-seed oil | *Reseda luteola* | 0·9358 | below − 15° |
| 2. NON-DRYING OILS (*Vegetable*). | | | |
| Almond oil | *Amygdalus communis* | 0·91844* | − 21° |
| Beech-nut oil | *Fagus sylvatica* | 0·923 | − 17·5° |
| Oil from seed of | *Butea frondosa* | 0·917 | + 10° |
| Oil from seed of | *Calophyllum inophyllum* | 0·942 | + 5° |
| Oil from seed of | *Canarium commune* | | + 5 to − 2·5° |
| Castor-oil | *Ricinus communis* | 0·9639* | − 18° |
| Cotton-seed oil | *Gossypium barbadense* | 0·9306 | |
| Colza-oil | *Brassica campestris oleifera* | 0·9136 at 15° | − 6·25° |
| Croton-oil | *Croton Tiglium* | 0·94263* | |
| Oil of Cyperus-grass | *Cyperus esculentus (root)* | 0·918 | |
| Oil of Daphne (*Oleum seminum Coccognidii*) | *Daphne Mezereum* | 0·914—0·921 | |
| Earth-nut oil | *Arachis hypogæa* | 0·918 | |
| Ergot-oil | *Secale cornutum* | 0·922 | − 37° |
| Hazel-nut oil | *Corylus Avellana* | 0·91987* | − 19° |
| Henbane-seed oil | *Hyoscyamus nigra* | 0·913* | |
| Horsechesnut oil | *Æsculus Hippocastanum* | 0·915 | + 8° |
| Mesua-oil | *Mesua ferrea* | 0·954 | + 5° |
| Black mustard oil | *Sinapis nigra* | 0·92102* | below 0° |
| White mustard oil | *Sinapis alba* | 0·93383* | does not solidify |
| Oil from seed of | *Nigella sativa* | 0·92 | + 2° |
| Oil from root and seed of | *Pinus quadrifolia* | 0·935 | |
| Parsley-oil | *Petroselinum sativum* | 1·078 at 12° | becomes turbid at − 12° but does not solidify |
| Plum-kernel oil | *Prunus domestica* | 0·9127 | − 8·7° |
| Oil from seed of | *Pongamia glabra* | 0·915 | + 8° |
| Summer Rape-seed oil | *Brassica præcox* | 0·91555* | |
| Winter Rape-seed oil | *Brassica Napus* | 0·91648* | a little below 0° |
| Sesamé-oil | *Sesamum orientale* | 0·92415* | − 5° |
| Spindle-tree oil | *Euonymus europæus* | 0·95717* | − 12° to − 15° |
| Spurge-oil | *Euphorbia Lathyris* | 0·92613* | − 11¼° |
| Oil from seed of | *Sterculia fœtida* | 0·923 | below + 3° |
| Oil from various kinds of | *Thea* and *Camellia* | 0·927 | forms an emulsion at 4·5° |

Cloez (*loc. cit.*) finds that drying oils, exposed to the air for 18 months, increase in weight by about 7 or 8 per cent. (10 grms. linseed oil increased to 10·703; 10 grms. poppy oil to 10·705; 10 grms. hemp oil to 10·778); non-drying oils, which thicken but slightly on exposure to air, gain from 3 to 5 per cent. (10 grms. olive oil increased to 10·372; almond oil to 10·459; castor oil to 10·268; horse-chesnut oil to 10·542); those which thicken considerably, such as rape, croton, and mustard oils, gain in the same time from 5 to 7 per cent.

3. FISH OILS. These are non-drying oils, obtained from fish and cetaceous animals: they have usually an offensive rancid odour, arising from the peculiar disposition above mentioned. When exposed to cold they for the most part deposit solid fats, palmitin, cetin, &c., while olein and other similar fats remain in the liquid state. Sperm oil yields by saponification, physetoleic acid and ethal, or cetylic alcohol. The most important of these oils are sperm oil, occurring, together with spermaceti, in certain cerebral cavities of the sperm-whale (*Physeter macrocephalus*); whale or train oil, from the blubber of *Balæna mysticetus* and other whales; seal oil; sea-calf oil; shark oil, from *Squalus maximus;* pilchard oil; porpoise oil, from *Dephinus phocæa;* dolphin oil, from *Delphinus globiceps;* cod-liver oil, from the liver of various species of *Gadus;* ray-liver oil, from the livers of *Raya clavata* and *R. batis;* and burbot oil, from the liver of *Gadus Lota* or *Lota vulgaris.* All these oils will be found described in their alphabetical places: cod-liver oil as OLEUM JECORIS ASELLI, dolphin-oil as DELPHIN (ii. 309).

4. OTHER ANIMAL OILS.—*a. Oil of Ants.* The residue left on distilling ants with water, yields by pressure a yellow or reddish-brown fatty oil, which floats on water and solidifies at a moderate degree of cold.

*β. Oils from Egg-yolk.*—The yolk of eggs hard boiled, and warmed, yields by pressure, and by exhaustion with ether, two fatty oils of different constitution. The oil obtained by pressure is reddish-yellow, viscid, neutral, and has little or no taste. It generally deposits a solid fat and solidifies at 4°—6° to a granular mass, which when left to drain on a filter leaves a solid fat melting at 56°. The oil freed from this fat is thicker than linseed oil, and solidifies to an amorphous mass at 0° (Planche, J. Pharm. i. 438). It contains $\frac{1}{300}$ of cholesterin (Lecanu, *ibid.* xv. i.); also volatile acids (Redtenbacher). The oil extracted by ether has a fine pure yellow colour, an acrid taste and an unpleasant odour, absorbs oxygen, and contains in addition to the true oil, a viscous substance similar to or identical with lecithin (iv. 566), which may be separated by filtration and pressure. The oil thus purified and likewise that which is extracted from the yolk by pressure, solidify at −6° to a granular mass containing cholesterin. Both oils, when exposed to the cold, deposit a mixture of margarin, cholesterin, and colouring matter. They are free from phosphorus and sulphur, and differ from other oils only by containing colouring matter and cholesterin. (Gobley, J. Pharm. [3] ix. 12.)

*γ. Lard oil.*—A nearly colourless oil obtained by pressing hog's lard, and used for greasing wool. Specific gravity, 0·915 (Chevreul) 100 pts. boiling alcohol dissolve 123 pts. of it. According to Braconnot, lard yields 0·62 of its weight of this oil.

*δ. Neat's-foot oil.*—The feet of oxen, after the hair and hoofs have been removed, yield when boiled with water a peculiar fatty matter, which after a while deposits a semi-solid fat leaving an oil which does not solidify at 0° C., and is not liable to become rancid. This oil is used for many purposes, especially for oiling church clocks.

*ε. Oil of Silkworms.*—Obtained by exhausting the caterpillars with alcohol and washing the extract with hot water. It is brownish-green; lighter than water; neutral; remains liquid at 0°; dissolves easily in cold alcohol and ether; is easily saponified by potash, less easily by lead-oxide, yielding stearic acid and a liquid acid, probably oleic. (Lassaigne, J. Chem. Med. xx. 471.)

*Adulteration of Fat oils.*—The difference in price of the several fat oils often gives rise to fraudulent admixtures; thus the best olive oil for table use is sometimes mixed with inferior oils, such as poppy, sesamé, or earth-nut oil; olive oil intended for manufacturing purposes is adulterated with colza oil; the latter, sometimes with poppy, linseed, or more often with whale oil, &c. The methods of detecting these adulterations are not very satisfactory.

Lefèbvre proposes to distinguish fat oils by their density, and has constructed for this purpose a hydrometer of peculiar construction, called an oleometer, having a very large cylindrical bulb and a very long stem, on which are inscribed densities from 0·8 to 0·94 for the temperature 15°, each density corresponding to that of a commercial oil, *e.g.* 0·917 to olive oil, 0·925 to poppy oil, 0·939 to linseed oil, &c. An ordinary centesimal alcoholometer may also be used for the purpose. The difference of density between different fat oils is, however, not sufficiently great to enable them to be

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detected with certainty in mixtures by such a method, moreover it has not been proved that the density of the oil obtained from any given source is really constant.

**Gobley** (J. Pharm [3] iv. 285; v. 67) limits the use of the hydrometer to the detection of poppy oil in olive and almond oils. For this purpose he used a hydrometer (*elæometer*) with very large bulb and thin stem. At the temperature of 12·5° C. the instrument sinks to zero in pure poppy oil, which is the densest of the three, and to 50° in pure olive oil, which is the lightest. The space between 0° and 50° is divided into 50 equal parts.

**Poutet** of Marseilles heats up the oil to be tested with one-twelfth of its weight of a solution of mercury in strong nitric acid. The nitrous acid or nitric peroxide evolved from this solution, converts the liquid olein into solid elaidin (ii. 368), causing the olive oil, if pure, to solidify completely after one or two hours' contact, whereas in presence of poppy oil or other drying oils, which are not solidified under the same circumstances, the solidification is retarded, and for a longer time in proportion to the quantity of drying oil present. In making these experiments, it is best to use strong nitric acid containing nitric peroxide; to agitate 2 or 3 cubic centimetres of this acid with the olive oil under examination; and to perform the same experiment on perfectly pure olive oil in a bottle of the same size. The two vessels are then left in a cellar, or a room the temperature of which does not exceed 10°, and the moment when the oil becomes thick enough to remain in the vessel on inversion is carefully observed. If the specimen under examination is pure, it will solidify at the same time as the other, but if it contains even 1 pt. in a hundred of poppy oil, its solidification will be retarded 40 minutes, and longer still for a larger quantity.

**Maumené** (Compt. rend. xxxv. 572) tests fat oils by the heat evolved on mixing them with strong sulphuric acid, poppy oil and drying oils in general being heated thereby much more strongly than olive oil; the mixture of poppy oil with sulphuric acid is likewise accompanied by a considerable evolution of sulphurous anhydride.

**Heydenreich** and **Penot** propose to distinguish the several fat oils by the colours which they exhibit in contact with strong sulphuric acid. When a drop of this acid is added to eight or ten drops of an oil placed on a plate of glass resting on white paper, the following colours are immediately produced:—*Olive oil* produces a deep yellow tint gradually becoming green; *Sesamé-oil* a bright red; *Colza oil* a greenish-blue aureola; *Poppy oil* becomes pale yellow with a dingy grey look; *Hemp oil* produces a distinct emerald-green tint; *Linseed oil* becomes brown-red, changing to black-brown.

The colours and other reactions exhibited in treating fat oils with various acids and alkaline reagents have also been examined by Professor F. C. **Calvert**, a summary of whose results is given in the table on page 183. The columns headed "+ Caustic Soda," indicate the results obtained on adding that alkali to an oil previously treated with the reagent at the head of the preceding column.

By these reactions it is possible, according to **Calvert**, to ascertain the presence of 10 per cent. of a given oil in many cases of adulteration; for example, poppy-oil in rape; olive in Gallipoli and India nut, as all of these assume a pale rose-colour: but when poppy-oil is mixed with olive or castor-oils there is a decrease in the consistency of the semi-saponified matter. [For details see Pharm. J. Trans. xiii. 356; also, *Ure's Dictionary of Arts*, &c. iii. 300.]

## B.—VOLATILE OILS.

*Essential oils. Essences. Ethereal oils. Distilled oils.*—These are compounds, either consisting wholly of carbon and hydrogen, or of the same elements with addition of smaller quantities of oxygen, sulphur, or nitrogen; of thin oily consistency at ordinary temperatures, and wholly volatile at higher temperatures; having a peculiar and generally pungent odour; very inflammable; sparingly soluble in water, but dissolving readily in alcohol and ether.

A large number of volatile oils occur ready formed in plants, and a smaller number in the animal body: others are produced by dry distillation of organic bodies—these are called **empyreumatic oils**, *e.g.* oil of amber, coal-oil, shale-oil, creasote, Dippel's oil, &c.; others by fermentation and other changes in the inodorous parts of plants (FERMENT OILS, ii. 634). Petroleum, rock-oil, mineral oil or mineral naphtha, must also be included amongst the oils produced by the decomposition of organic bodies (see NAPHTHA, p. 2, and PETROLEUM). Volatile oils are also produced by the action of sulphuric or phosphoric acid on organic bodies, *e.g.* oil of wine by distilling alcohol in excess of sulphuric acid, menthene (iii. 880) by distilling peppermint-camphor with phosphoric acid. In this article we shall consider only the volatile oils existing ready

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*Reactions of Fat Oils with Acids and Alkalis.*

| Oils. | Caustic Soda. Sp. gr. 1·340. | Sulphuric Acid. Sp. Gr. 1·475. | Sulphuric Acid. Sp. Gr. 1·530. | Sulphuric Acid. Sp. Gr. 1·635. | Nitric Acid. Sp. Gr. 1·180. | Nitric Acid. Sp. Gr. 1·220. | Nitric Acid. Sp. Gr. 1·33. | + Caustic Soda. Sp. Gr. 1·340. | Phosphoric Acid. Syrupy. | Sulphuric Acid + Nitric Acid. | Aqua Regia. | + Caustic Soda. Sp. Gr. 1·340. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Olive . . . . . | Slight yellow. | Green tinge. | Greenish-white. | Light green. | Greenish. | Greenish. | Greenish. | Fluid white mass. | Slight green. | Orange-yellow. | . . | Fluid white mass. |
| Gallipoli . . . . | Ditto. | Ditto. | Grey. | Brown. | Ditto. | Ditto. | Ditto. | Fibrous ditto. | Ditto. | Dark brown. | . . | Fibrous yellowish-white mass. |
| India nut . . . . | Thick and white. | . . | Dirty white. | Light brown. | . . | . . | . . | Ditto. | . . | Orange-white. | . . | Fibrous white mass. |
| Pale rapeseed . . . | Dirty yellowish-white. | . . | Pink. | Brown. | . . | . . | . . | Fluid ditto. | . . | Dark brown. | . . | Fibrous yellowish-white mass. |
| Poppy . . . . | Ditto. | . . | Dirty white. | . . | . . | Orange-yellow. | Red. | Light red fluid mass. | . . | Slight yellow. | . . | Fluid intense rose-coloured mass. |
| French nut . . . | Ditto. | Brownish. | Grey. | Brown. | Yellow. | Red. | Dark red. | Fibrous red mass. | Brown-yellow. | Dark brown. | Yellow. | Fibrous orange-mass. |
| Sesame . . . . | Ditto. | Green tinge. | Greenish dirty white. | . . | Orange-yellow. | Ditto. | Ditto. | Fluid red mass, with brown liquor underneath. | . . | Green becoming intense red. | Ditto. | Fluid orange mass with brown liquor beneath. |
| Castor . . . . | White. | . . | Dirty white. | . . | . . | . . | . . | Fibrous white mass. | . . | Brownish-red. | . . | Fibrous pale rose-coloured mass. |
| Hempseed . . . | Thick brownish-yellow. | Intense green. | Intense green. | Intense green. | Dirty green. | Greenish dirty brown. | Greenish dirty brown. | Fibrous light brown mass. | Green. | Green becoming black. | Green. | Fibrous light brown mass. |
| Linseed . . . . | Fluid yellow. | Green. | Dirty green. | Green. | Yellow. | Yellow. | Green becoming brown. | Fluid yellow mass. | Brown yellow-green. | Ditto. | Greenish-yellow. | Fluid orange mass. |
| Lard . . . . . | Pinkish-white. | Dirty white. | Dirty white. | Light brown. | . . | . . | Very slight yellow. | Fluid mass | . . | Brown. | . . | Fluid pink mass. |
| Neat's-foot . . . | Dirty yellowish-white. | Yellow tinge. | Brownish dirty white. | Brown. | Light yellow. | Light yellow. | Light brown. | Fibrous white mass. | . . | Dark brown. | Slight yellow. | Fibrous brownish-yellow mass. |
| Sperm . . . . | Dark red. | Light red. | Red. | Intense brown. | Slight yellow. | Ditto. | Red. | Fluid mass. | Dark red. | Ditto. | Ditto. | Fluid orange-yellow mass. |
| Seal . . . . . | Ditto. | Ditto. | Ditto. | Ditto. | Pink. | Light red. | Ditto. | Ditto. | Ditto. | Ditto. | Ditto. | Ditto. |
| Cod-liver . . . . | Ditto. | Purple. | Purple. | Ditto. | . . | . . | Ditto. | Ditto. | Ditto. | Ditto. | Yellow. | Ditto. |

formed in the vegetable or animal organism, which are especially distinguished as essential oils.

Only a few volatile oils have been obtained from the animal body—the oils of ants, castoreum and ambergris for example—and these have been but little studied, though similar compounds might doubtless be obtained from many other odorous animal products. But the great source of volatile oils is the vegetable kingdom, where they occur in very large quantity and in almost all parts of the plant, as in the wood and bark of the stem and root; under the epidermis of the leaves, calyces, petals, fruit, &c.; in the different coatings of the seed and in the cellular tissue of the seed-vessels; rarely in the albumen, sometimes even in the embryo of the seed.

These vegetable oils or essences consist either wholly of hydrocarbons, or of mixtures of hydrocarbons with compounds of carbon, hydrogen, and oxygen. Those which exist ready formed in plants do not appear to contain any other element. Sulphur is found only in certain oils resulting from a kind of fermentation-process, as in the volatile oils of mustard and garlic; nitrogen, when it occurs, must be regarded as an impurity resulting from admixed vegetable tissue. Many vegetable essential oils when exposed to cold are separated into a solid compound, called a camphor or stearoptene, and a liquid oil, which for distinction is sometimes called an elæoptene.

The following are the modes of extracting essential oils from plants:—

1. *By Pressure.*—This method succeeds only with certain parts of plants which are very rich in oil, such as lemon and orange-peel.

2. *By Distillation*, generally with addition of water.—Heating without water is apt to produce charring and admixture of empyreumatic oils. The substances containing the volatile oil are either mixed with water in a large still or retort, and distilled after sufficient maceration; or they are placed in the dry state on the upper perforated base of the still, and subjected to the action of vapour of water. Although the boiling point of most volatile oils is above that of water, they nevertheless volatilise at 100°, in consequence of the diffusion of the oil-vapour into the vapour of water produced at that temperature. In the distillation of the less volatile oils, however, it is usual to add common salt to the water, in order to raise the temperature a few degrees, and thereby increase the tendency of the oil to pass over with the aqueous vapour. The vapours condense in the cooling tube or receiver, which is kept cold for the purpose; and the water takes up as much of the oil as it is capable of dissolving. If the quantity of oil present is more than sufficient to saturate the water, the excess separates out; in the contrary case, the distillate is *cohobated;* that is to say, the water containing the oil in solution is distilled with a fresh quantity of the substance which contains the oil, and thereby made to take up a double quantity of oil. A more abundant product is likewise obtained by distilling the original vegetable substance, not with pure water, but with water which has previously been used for the same distillation, and is therefore saturated with oil.—If the oil which passes over readily solidifies, the cooling tube must not be kept at too low a temperature.—The oil which collects either at the top or at the bottom of the water is separated by mechanical means.

Many plants yield a larger quantity of oil after drying; and when distilled in the fresh state, with cold water, they yield a comparatively large quantity of oil together with turbid water; but if covered with boiling water and then distilled, they yield clear water and less oil. The cause of this difference is, that when the plant is dried, or immersed in cold water containing air, the oil oxidises, and is thereby rendered less soluble in water; hence it forms a poorer and turbid solution, and for the most part separates out. (Desmarest, J. Pharm. 19, 163; abstr. Ann. Pharm. 9, 291.)

Volatile oils obtained by distillation, and likewise the water which passes over with them, have at first an unpleasant, empyreumatic odour, which, however is not permanent.

3. Many strongly smelling parts of plants yield no volatile oil, even by repeated cohobation with water, probably because the quantity contained in them is too small, or because the oil is too soluble in water, or too much inclined to decompose by the action of air and heat; *e.g.* the flowers of many kinds of *Narcissus* and *Hyacinth;* of *Polyanthes Jonquilla, Viola odorata, Jasminum off., Philadelphus coronarius, Tilia europæa, Reseda odorata, Heliotropium europæum.* Such flowers, placed in layers between cotton soaked in olive oil, impart their perfume to the oil.

From some of them it has been found possible to extract the odoriferous principle in the separate state. Robiquet (J. Pharm. xxi. 334) exhausted the fresh corollas of *Polyanthes Jonquilla* with ether in compression-filters; separated the upper yellow ethereal stratum of liquid from the lower watery layer; distilled the ether from the upper liquid at a gentle heat; and obtained a residue consisting of crystalline nodules, together with a mother-liquid, which, when evaporated in the air gave off a strong and agreeable odour of jonquils. The crystalline nodules, when purified, formed an inodorous camphor; and appeared to be the odoriferous oil converted into this camphor by exposure to the air. L. A. Buchner (N. Br. Arch. viii. 70) obtained similar results by applying Robiquet's process to the flowers of *Philadelphus*, *Tilia*, and *Reseda*.

4. The less volatile oils, and more especially the camphors, are likewise frequently extracted by alcohol or ether, from which they are afterwards separated by evaporation and cooling.

Many gum-resins, such as myrrh, do not yield the oil which they contain, or at least yield it very imperfectly, by distillation with water, because it is enveloped in gummy matters. To extract the oil from these gum-resins, they are pulverised and then exhausted three times with an equal quantity of cold alcohol, agitating frequently, and leaving the whole to stand for some time; the filtered tincture is then poured into a tubulated retort, both apertures of which are left open, and left for some months at a temperature of 12°—21°, till the greater part of the alcohol is evaporated (if heat were applied, the oil would likewise pass over). The turpentine-like residue is then covered with water, and distilled after twelve hours, whereupon the oil passes over in abundance. (Bonastre, J. Pharm. xvii. 108.)

The product obtained by either of these three modes of preparation rarely consists of a simple volatile oil, but generally of a mixture of two or more oils. The lighter and more volatile of these is usually a pure hydrocarbon; the other is either an oil containing oxygen, or a camphor. These bodies are sometimes distinguished by their melting points: thus, a volatile oil, properly so-called, often holds a camphor in solution, and the latter crystallises out on cooling, especially if part of the volatile oil (which is more easily vaporised) has been previously driven off. Sometimes again they are distinguished by their different volatility; when such a mixture is distilled, the boiling point is at first low, but rises as the quantity of the more volatile oil in the residue diminishes, till at length, when the whole of the latter has passed over (together with a considerable quantity of the more fixed oil), the boiling point no longer rises, but remains constant. In such cases, the more volatile oil generally consists wholly of carbon and hydrogen, while the more fixed oil likewise contains oxygen The former may be distilled without decomposition over fused hydrate of potassium;. but the more fixed oil when thus treated, takes up an additional quantity of oxygen from the water of the hydrate of potassium (liberating the hydrogen), and is converted into an acid which remains combined with the potash. Hence to separate the non-oxygenated oil from such a mixture, it is partly distilled so as to leave behind the greater part of the more fixed oil, and the portion which first passes over is made to drop slowly through the tubulure of another retort upon hydrate of potassium kept in a state of fusion; the non-oxygenated oil then passes over pure. (Gerhardt and Cahours, Ann. Ch. Phys. [3] 61.)

If a volatile oil has been partly converted into a resin by continued exposure to the air, it may be freed from the resin by distillation with water. Any moisture which adheres to the oil may be removed by continued agitation with chloride of calcium, and subsequent distillation.

*Properties.*—Volatile oils differ considerably in colour. Many are perfectly colourless when pure, others are yellow, red or brown, and a few are green or blue. All of them have powerful odours, some agreeable, others repulsive, and a sharp burning aromatic taste; some of them produce a feeling of coolness on the tongue. They are not greasy to the touch like fat oils, but rather make the skin brittle and rough. Their specific gravity varies from 0·847 to 1·096; but the greater number are lighter than water. Their solidifying points are very unequal, some solidifying at 0°, others requiring a much lower temperature, while others again remain solid a few degrees above 0°. Most of them, when exposed to a low temperature, deposit a solid camphor or stearoptene (p. 184). Most volatile oils properly so called, boil between 150° and 200°; oil of copaiba at 260°; and several camphors between 300° and 400°.

Volatile oils possess great refractive and dispersive power, and exhibit great diversity in their action on polarised light, some being dextro-, others lævo-rotatory in very various degrees, while a few are inactive. The following table exhibits the rotatory power of a considerable number of volatile oils, together with their refractive indices for the lines A, D, and H, as determined by Gladstone (Chem. Soc. J. xvii. 3), also their specific gravities. The rotatory power was determined for a column of liquid 10 inches long; the same length of a solution of equal parts of cane-sugar and water produces a deviation of + 105°.

The blue or green colour exhibited by certain volatile oils, chiefly from plants of the Composite order, wormwood and chamomile for example, is due to an oily compound of a very deep blue colour, called cœrulein, which may be separated by distillation, going over with the last portions of the oil, but has not been obtained pure. The solution of this blue substance in oils or alcohol exhibits, when examined by a hollow wedge and prism (Light, iii. 638), a very characteristic spectrum, in which the orange and yellow rays are first absorbed, and at a certain depth nothing is

*Specific Gravities and Optical Properties of Essential Oils.*

| Crude Oils. | Spec. Grav. at 15·5° C. | Refractive Indices. | | | | Rotation. |
|---|---|---|---|---|---|---|
| | | Temp. | A. | D. | H. | |
| Anise | ·9852 | 16·5° | 1·5433 | 1·5566 | 1·6118 | − 1° |
| Atherosperma moschatum | 1·0425 | 14° | 1·5172 | 1·5274 | 1·5628 | + 7° |
| Bay | ·8808 | 18·5° | 1·4944 | 1·5022 | 1·5420 | − 6° |
| Bergamot | ·8825 | 22° | 1·4559 | 1·4625 | 1·4779 G. | + 23° |
| „ Florence | ·8804 | 26·5° | 1·4547 | 1·4614 | 1·4760 G. | + 40° |
| Birch-bark | ·9005 | 8° | 1·4851 | 1·4921 | 1·5172 | + 38° |
| Cajeput | ·9203 | 25·5° | 1·4561 | 1·4611 | 1·4778 | 0° |
| Calamus | ·9388 | 10° | 1·4965 | 1·5031 | 1·5204 G. | + 43·5° |
| „ Hamburg | ·9410 | 11° | 1·4843 | 1·4911 | 1·5144 | + 42°? |
| Caraway | ·8845 | 19° | 1·4601 | 1·4671 | 1·4886 | + 63° |
| „ Hamburg 1st dist. | ·9121 | 10° | 1·4829 | 1·4903 | 1·5142 | |
| „ „ 2nd | ·8832 | 10·5° | . . | 1·4784 | | |
| Cascarilla | ·8956 | 10° | 1·4844 | 1·4918 | 1·5158 | + 26° |
| Cassia | 1·0297 | 19·5° | 1·5602 | 1·5748 | 1·6243 G. | 0° |
| Cedar | ·9622 | 23° | 1·4978 | 1·5035 | 1·5238 | + 3° |
| Cedrat | ·8584 | 18° | 1·4671 | 1·4731 | 1·4952 | + 156° |
| Citronella | ·8908 | 21° | 1·4599 | 1·4659 | 1·4866 | − 4° |
| „ Penang | ·8847 | 15·5° | 1·4604 | 1·4665 | 1·4875 | − 1° |
| Cloves | 1·0475 | 17° | 1·5213 | 1·5312 | 1·5666 | − 4° |
| Coriander | ·8775 | 10° | 1·4592 | 1·4652 | 1·4805 G. | + 21°? |
| Cubebs | ·9414 | 10° | 1·4953 | 1·5011 | 1·5160 G. | |
| Dill | ·8922 | 11·5° | 1·4764 | 1·4834 | 1·5072 | + 206° |
| Elder | ·8584 | 8·5° | 1·4686 | 1·4749 | 1·4965 | + 14·5° |
| Eucalyptus amygdalina | ·8812 | 13·5° | 1·4717 | 1·4788 | 1·5021 | − 136° |
| „ oleosa | ·9322 | 13·5° | 1·4661 | 1·4718 | 1·4909 | + 4° |
| Indian geranium | ·9043 | 21·5° | 1·4653 | 1·4714 | 1·4868 G. | − 4° |
| Lavender | ·8903 | 20° | 1·4586 | 1·4648 | 1·4862 | − 20° |
| Lemon | ·8498 | 16·5° | 1·4667 | 1·4727 | 1·4946 | + 164° |
| Lemon grass | ·8932 | 24° | . . | 1·4705 | . . | − 3°? |
| „ Penang | ·8766 | 13·5° | 1·4756 | 1·4837 | 1·5042 | 0° |
| Melaleuca ericifolia | ·9030 | 9° | 1·4655 | 1·4712 | 1·4901 | + 26° |
| „ linarifolia | ·9016 | 9° | 1·4710 | 1·4772 | 1·4971 | + 11° |
| Mint | ·9342 | 19° | 1·4767 | 1·4840 | 1·5015 G. | − 116° |
| „ | ·9105 | 14·5° | 1·4756 | 1·4822 | 1·5037 | − 13° |
| Myrtle | ·8911 | 14° | 1·4623 | 1·4680 | 1·4879 | + 21° |
| Myrrh | 1·0189 | 7·5° | 1·5196 | 1·5278 | 1·5472 G. | − 136° |
| Neroli | ·8789 | 18° | 1·4614 | 1·4676 | 1·4835 G. | + 15° |
| „ | ·8743 | 10° | 1·4673 | 1·4741 | 1·4831 F. | + 28° |
| Nntmeg | ·8826 | 24° | 1·4644 | 1·4709 | 1·4934 | + 44° |
| „ Penang | ·9069 | 16° | 1·4749 | 1·4818 | 1·5053 | + 9° |
| Orange-peel | ·8509 | 20° | 1·4633 | 1·4699 | 1·4916 | + 32°? |
| „ Florence | ·8864 | 20° | 1·4707 | 1·4774 | 1·4980 | + 216° |
| Parsley | ·9926 | 8·5° | 1·5068 | 1·5162 | 1·5417 G. | − 9° |
| Patchouli | ·9554 | 21° | 1·4990 | 1·5050 | 1·5194 G. | |
| „ Penang | ·9592 | 21° | 1·4980 | 1·5040 | 1·5183 G. | − 120° |
| „ French | 1·0119 | 14° | 1·5074 | 1·5132 | 1·5202 F. | |
| Peppermint | ·9028 | 14·5° | 1·4612 | 1·4670 | 1·4854 | − 72° |
| „ Florence | ·9116 | 14° | 1·4628 | 1·4682 | 1·4867 | − 44° |
| Petit grain | ·8765 | 21° | 1·4536 | 1·4600 | 1·4808 | + 26° |
| Rose | ·8912 | 25° | 1·4567 | 1·4627 | 1·4835 | − 7° |
| Rosemary | ·9080 | 16·5° | 1·4632 | 1·4688 | 1·4867 | + 17° |
| Rosewood | ·9064 | 17° | 1·4843 | 1·4903 | 1·5113 | − 16° |
| Santalwood | ·9750 | 24° | 1·4959 | 1·5021 | 1·5227 | − 50° |
| Thyme | ·8843 | 19° | 1·4695 | 1·4754 | 1·4909 G. | |
| Turpentine | ·8727 | 13° | 1·4672 | 1·4732 | 1·4938 | − 79° |
| Verbena | ·8812 | 20° | 1·4791 | 1·4870 | 1·5059 G. | − 6° |
| Wintergreen | 1·1423 | 15° | 1·5163 | 1·5278 | 1·5737 | + 3° |
| Wormwood | ·9122 | 18° | 1·4631 | 1·4688 | 1·4756 F. | |

suffered to pass except the greenish-blue rays and the extreme red band. A diagram of this spectrum is given in Gladstone's paper just referred to, p. 14.

Most of the essential oils existing ready formed in plants contain hydrocarbons of the formula $nC^{10}H^{16}$. Some, as the oils of turpentine, lemon, cubebs and copaiba, consist wholly of these hydrocarbons; others contain also oxidised compounds; oil of wintergreen, for example, is a mixture of a hydrocarbon, $C^{10}H^{16}$, with methyl-salicylic ether. These hydrocarbons are separated by fractional distillation as above mentioned, passing over at the beginning of the process, and are further purified by rectification over sodium. The following table (p. 188) exhibits the densities and optical properties of a considerable number of these polymeric hydrocarbons. The oils are arranged according to their specific gravities at 20° C. The column headed "Dispersion at 20° C." gives the difference between the refractive indices of the lines H and A. The "sensitiveness" is the amount of diminution of the refractive index when the temperature rises 10°; it is calculated for the line A, and the number 48 is an abbreviation of 0·0048. The "specific refractive energy" is the refractive index, minus unity, divided by the density (LIGHT, iii. 625). In the following table it is taken for A, that is the column represents $\frac{\mu_A - 1}{D}$.

These hydrocarbons may be divided into two great groups, the line of separation being between those from rosemary and cloves. The first group, with a lower specific gravity, has always a far lower boiling point, a smaller index of refraction, and a higher sensitiveness; it has also on the whole a smaller dispersion. The specific refractive energy, however, of the two groups is about the same. The hydrocarbons of the first group are also generally more limpid, and dissolve more freely in aqueous alcohol.

These large groups are further capable of subdivision. The first ten hydrocarbons in the table resemble one another very closely. Indeed, it is probable that the three which are derived from the peel of the orange, citron, and lemon respectively, should be considered as identical rather than isomeric; and it is not unlikely that some of the others are the same body from different plants. Gaultherilene, carvene, and the hydrocarbon from nutmeg, form a small group, if indeed they are not identical. The hydrocarbons from wormwood, anise, thyme, mint, and laurel-turpentine, group with ordinary turpentine; bay, myrtle, and rosemary stand alone, each having a low refraction and dispersion, but they differ much in specific gravity. Peppermint is somewhat intermediate in its properties. Terebene and the hydrocarbons from parsley and *Eucalyptus amygdalina* give high refractive indices. It is possible that some of these last contain a small quantity of some hydrocarbon of another type but nearly the same composition.

Again, the second large group with the higher specific gravities is capable of subdivision. The hydrocarbons from cloves and rosewood appear nearly, if not quite, identical in properties, and are certainly different from patchouli, calamus, and cascarilla.

Colophene differs from the second large group in much the same way as that differs from the first, though to a smaller extent.

All the members of the first great group, with the boiling points included between 160° and 176°, have the formula $C^{20}H^{16}$, which is usually assigned to oil of turpentine on the ground of its vapour-density and compounds with the hydracids.

All the members of the second great group, with boiling points included between 249° and 260° C., have the formula $C^{30}H^{24}$, which is assigned to oil of cubebs from its compound with hydrochloric acid.

Colophene with a boiling point of 315° C., has long had the formula $C^{40}H^{32}$ assigned to it.

The specific refractive energy is a property of bodies intimitely connected with their ultimate composition, and it might be expected that, notwithstanding diversities of boiling point and density, this property would be the same for the different isomeric hydrocarbons. Yet though the differences are not great they seem to be real, for the lemon group is uniformly about 0·549 and the turpentine group about 0·536.

The phenomena of circular polarisation are not of much use in the classification of hydrocarbons, or as a means of distinction between the crude oils; for it is found that different samples of the same hydrocarbon, or of the same oil, which closely resemble one another in other respects, frequently differ widely in respect of this property. It may be observed, however, that the hydrocarbons of the great lemon-group exhibit the highest rotatory power, and always to the right, excepting that from cascarilla, which belongs to the same group, but is nevertheless quite inactive.

*Decompositions of Volatile Oils.*—1. Those oils which have a high boiling-point are partly decomposed by simple *distillation*, leaving a residue of charcoal; but when distilled with water, or gently heated in the air, they may be volatilised without decom-

*Specific Gravities, Boiling Points, and Optical Properties of Hydrocarbons from Essential Oils* (Gladstone).

| Source of Hydrocarbon. | Specific gravity at 20° C. | Boiling point. | Refractive index A, at 20° C. | Dispersion at 20° C. | Sensitiveness. | Specific refractive energy. | Rotation. |
|---|---|---|---|---|---|---|---|
| Orange-peel | ·8460 | 174°C. | 1·4645 | ·0277 | 48 | ·5490 | +154° |
| ,, Florence | ·8468 | 174° | 1·4650 | ·0281 | 49 | ·5491 | +260° |
| Cedrat | ·8466 | 173° | 1·4650 | ·0280 | 49 | ·5492 | +180° |
| Lemon | ·8468 | 173° | 1·4660 | ·0280 | 49 | ·5502 | +172° |
| Bergamot | ·8466 | 175° | 1·4619 | ·0295 | 49 | ·5456 | + 76° |
| ,, Florence | ·8464 | 176° | 1·4602 | ·0287 | 48 | ·5437 | + 82° |
| Neroli | ·8466 | 173° | 1·4614 | ·0291 | 47 | ·5450 | + 76° |
| Petit grain | ·8470 | 174° | 1·4617 | ·0282 | 46 | ·5439 | + 60° |
| Caraway, Hamburg, 1st dist. | ·8466 | 176° | 1·4645 | ·0286 | 48 | ·5486 | +180° |
| Dill | ·8467 | 173° | 1·4646 | ·0288 | 46 | ·5486 | +242° |
| Cascarilla | .8467 | 172° | 1·4652 | ·0305 | 49 | ·5494 | 0° |
| Elder | ·8468 | 172° | 1·4631 | ·0269 | 47 | ·5468 | + 15° |
| Bay | ·8508 | 171° | 1·4542 | ·0260 | 47 | ·5338 | − 22° |
| Gaultherilene | ·8510 | 168° | 1·4614 | ·0271 | 49 | ·5422 | |
| Nutmeg | ·8518 | 167° | 1·4630 | ·0284 | 47 | ·5435 | + 49° |
| ,, Penang | ·8527 | 166° | 1·4634 | ·0274 | 49 | ·5434 | + 4° |
| Carvene | ·8530 | 166° | 1·4610 | ·0261 | 48 | ·5440 | − 20° |
| ,, Hamburg, 2nd dist. | ·8545 | . . | 1·4641 | ·0263 | 48 | ·5431 | + 86° |
| Wormwood | ·8565 | 160° | 1·4590 | ·0253 | 47 | ·5359 | + 46° |
| Terebene | ·8583 | 160° | 1·4670 | ·0275 | 48 | ·5440 | 0° |
| Anise | ·8580 | 160° | 1·4607 | ·0268 | 47 | ·5368 | |
| Mint | ·8600 | 160° | 1·4622 | ·0255 | 48 | ·5374 | + 30° |
| Peppermint | ·8602 | 175° | 1·4577 | ·0267 | 47 | ·5321 | − 60° |
| Laurel turpentine | ·8618 | 160° | 1·4637 | ·0260 | 47 | ·5380 | + 94° |
| Thyme | ·8635 | 160° | 1·4617 | ·0282 | 48 | ·5346 | − 75° |
| Turpentine I. | ·8644 | 160° | 1·4612 | ·0250 | 47 | ·5335 | + 48° |
| ,, II. | ·8555 | 160° | 1·4590 | ·0256 | 47 | ·5365 | − 87° |
| ,, III. | ·8614 | 160° | 1·4621 | ·0249 | . . | ·5364 | − 90° |
| ,, IV. | ·8600 | 160° | 1·4613 | ·0254 | 47 | ·5364 | − 88° |
| Eucalyptus amygdalina | ·8642 | 171° | 1·4696 | ·0323 | 49 | ·5434 | −142° |
| Myrtle | ·8690 | 163° | 1·4565 | ·0248 | 47 | ·5253 | + 64° |
| Parsley | ·8732 | 160° | 1·4665 | ·0291 | 46 | ·5355 | − 44° |
| Rosemary | ·8805 | 163° | 1·4583 | ·0241 | 46 | ·5205 | + 8° |
| Cloves | ·9041 | 249° | 1·4898 | ·0284 | 45 | ·5417 | |
| Rosewood | ·9042 | 249° | 1·4878 | ·0277 | 45 | ·5395 | − 11° |
| Cubebs | ·9062 | 260° | 1·4950 | ·0302 | 41 | ·5462 | + 59° |
| Calamus | ·9180 | 260° | 1·4930 | ·0322 | 42 | ·5370 | + 55° |
| ,, Hamburg | ·9275 | 260° | 1·4976 | ·0337 | 43 | ·5365 | + 22° |
| Cascarilla | ·9212 | 254° | 1·4926 | ·0307 | 42 | ·5347 | + 72° |
| Patchouli | ·9211 | 254° | 1·4966 | ·0274 | 42 | ·5391 | |
| ,, Penang | ·9278 | 257° | 1·4963 | ·0275 | 44 | ·5349 | − 90° |
| ,, French | ·9255 | 260° | 1·5009 | ·0262 | 42 | ·5412 | |
| Colophene | ·9391 | 315° | 1·5084 | ·0309 | 41 | ·5413 | 0° |

position. But even the more volatile oils, when mixed with earthy substances, such as clay, chalk, sand, &c., which mechanically prevent their volatilisation, are partially decomposed by distillation, combustible gases being evolved, and charcoal left behind; if they contain oxygen, they may likewise yield carbonic oxide, acetic acid, &c. When the vapour of a volatile oil is passed through a red-hot tube, it is resolved into combustible gases and charcoal, which is sometimes finely divided, sometimes shining, dense, and difficult to burn; the portion of the oil which has passed over undecomposed is often found to be altered in its properties, as, for example, in its boiling point.—2. Volatile oils are very inflammable, and burn with a clear flame which deposits a large quantity of soot. If the vapour of a volatile oil be made to issue from a fine jet, under a pressure of 1–6 centimetres of mercury, it does not take fire till it has reached a distance of some centimetres from the jet; that is to say, till it has become mixed with four or five times its volume of air; it burns with a bright flame, which no longer smokes, and may be used for illumination.—3. Essential oils, when placed in vessels not perfectly closed, and at the medium temperature of the air,

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absorb oxygen gas; acquire the power of reddening litmus strongly, from formation of benzoic, cinnamic, acetic, and other organic acids; and are then partially converted into resins, becoming viscid and less odoriferous, and passing from the colourless state to yellow or red-brown, or from blue to brown. Oils thus altered are resolved by distillation into pure oil and a residue of resin. The absorption of oxygen takes place with different degrees of rapidity in different oils. For the first few days it goes on slowly, then increases in rapidity up to a certain limit, beyond which it again diminishes, and after several months becomes imperceptible. During this change, and especially towards the end, the oil exhales a small quantity of carbonic anhydride, and a still smaller quantity of hydrogen. At the same time, a small quantity of very acid water is produced, which is loosely attached to the resinised oil, but may be separated from it either by the application of heat or by exposure to the sun.—4. A similar decomposition to that which takes place in the air, is likewise produced by placing the oil in contact with *nitrous gas*, which it rapidly absorbs; also by boiling the oil with *oxide of copper* or *peroxide of lead*, water being then formed; or by digesting it with *mercuric nitrate* or *chloride*, these bodies being thereby converted into mercurous nitrate and calomel respectively. Volatile oils are likewise resinised by *stannic chloride* and *pentachloride of antimony*, the latter often yielding reduced metal. Oils which easily resinise in the air are likewise immediately thickened by agitation with a warm concentrated solution of *neutral ferric sulphate*.—5. Volatile oils absorb *chlorine gas*, with evolution of heat, and are converted into viscid substances (Thénard). Hydrochloric acid is frequently formed in this reaction, a substitution of chlorine for hydrogen likewise taking place. *Bromine* exhibits similar reactions (Laurent).—6. Many volatile oils proper give up their hydrogen to *iodine* so rapidly, and with so great a development of heat, that an explosion takes place accompanied with evolution of violet and yellow vapours. This is the case with the oils of turpentine, juniper, savine, lemon, rosemary, and lavender. The residue is a thickened oil or a brown acid resin. These oils lose by age the property of deflagrating with iodine.—Other oils dissolve iodine quickly, with or without evolution of heat, forming therewith a brown, thickish oil, or a soft or hard resin, with separation of a brown liquid containing hydriodic acid. Such is the case with the oils of cinnamon, sassafras, cloves, rue, tansy, caraway, fennel, and peppermint.—7. *Fuming nitric acid* decomposes essential oils mostly with great rapidity, the action being attended with evolution of gas, and with development of heat often amounting to the most vivid inflammation; those essential oils which are not set on fire by fuming nitric acid, generally burst into flame when treated with nitric acid to which half its bulk of sulphuric acid has been added. After the combustion, a residue of charcoal is left. If, however, the oil does not take fire, there remains a soft, bitter resin, which retains nitric peroxide, even after long washing with water, and a yellow or brown acid liquid from which water still separates a resinous substance. Camphors are not so rapidly decomposed; several of them and of other volatile oils are converted by heating with dilute nitric acid, partly into peculiar acids (benzoic and anisic acids), partly into oxalic acid. Many oils turn yellow when mixed with one-fourth to one-half their weight of concentrated nitric acid; others first turn pale red, then bright red, and after twenty-four hours, brown; others, again, acquire a beautiful violet colour (Bonastre).—8. Strong *sulphuric acid* mixes with most essential oils, causing rise of temperature and evolution of sulphurous anhydride, together with a volatile oil which smells of strawberries; the product is a thick brown liquid, from which water, in many cases, separates an isomeric compound (*e. g.* anisoïn from anise-oil); in other cases, a brown acid substance, which behaves, sometimes like artificial tannin, sometimes like an acid resin, dissolves in alcohol and alkalis, and, to a certain extent, also in water: heating the sulphuric acid solution causes the mass to carbonise. Camphors, which usually dissolve without decomposition in cold sulphuric acid, likewise become charred when heated with it.

*Combinations*.—*a*. Essential oils and many camphors are slightly soluble in *water*, to the extent of about 1 pt. in 1,000; those which contain oxygen dissolve more freely than those which do not. The solution is sometimes obtained by agitating the volatile oil with water, but more frequently by distilling the water with substances which contain the volatile oil. The products are called *Distilled Waters* (*Aquæ distillatæ*). They are transparent and colourless, unless the oil is in excess, in which case it remains for a long time suspended in the liquid and renders it turbid; they possess the taste and smell of the volatile oils which they contain. Agitation with a fixed oil (Davies, J. Pharm. ix. 16), or with ether, withdraws the volatile oil from the water, and on evaporating the ethereal solution, the greater part of the oil is left behind (Soubeiran, J. Pharm. xvii. 620; xix. 50). Agitating the water with common salt separates a considerable portion of the oil; such is the case with *Aqua Fœniculi*, *Menthæ piperitæ*, and *Cinnamomi*, and with water containing primrose-camphor. (Hünefeld, J. pr. Chem. ix. 24.)

To determine the quantity of volatile oil contained in a distilled water, half an ounce of the liquid is to be mixed with a small quantity of gelatinous starch, and a solution of 1 grain of iodine in 500 grains of alcohol and 1,500 grains of water added, with agitation, till the oil ceases to give up hydrogen to the iodine, and consequently the iodine begins to impart a blue colour to the starch. It must, however, be observed, that different oils destroy the blueing properties of different quantities of iodine, and that therefore this mode of testing can be applied only for comparing different samples of the same kind of distilled water one with the other.

*β.* Volatile oils dissolve readily in *alcohol*, and most of them mix with absolute alcohol in all proportions. According to Saussure, the solubility of different oils increases with the quantity of oxygen which they contain; hence also the same oil is more readily soluble the longer it has been exposed to the air. Such solutions are obtained by distilling parts of plants which contain the volatile oil with alcohol and a small quantity of water, which prevents charring towards the end of the distillation. Many of the preparations which apothecaries call "Spirits" are solutions of this kind, as also *perfumed waters*, such as *Eau de Cologne*, *Lavender-water*, &c. Most camphors also dissolve readily in alcohol; there are but few which dissolve with difficulty. All these solutions burn with a bright flame, which is smoky if the solution contains much oil. When mixed with water, they turn milky, from separation of the oil, part of which, however, remains dissolved in the aqueous mixture. If a volatile oil is mixed with only a small quantity of alcohol, it does not become turbid when mixed with water, and only gives up its alcohol when repeatedly agitated with fresh quantities of water.

*Wood-spirit* and *acetone* behave like alcohol; so likewise do *ether* and several other ethereal liquids, excepting that from the latter the oils cannot be separated by water. *Sulphide of carbon* mixes in all proportions with volatile oils, and dissolves camphors.

Volatile oils mix with *fats*, dissolve most *resins* and *resinous colouring matters*, and several *organic bases;* they also mix with one another.

With the aid of heat, they dissolve a tolerably large quantity of *phosphorus*, forming a liquid which shines in the dark, and deposits the greater part of the phosphorus on cooling.

They also, when heated, dissolve a small quantity of *sulphur*, which crystallises out again on cooling; when boiled for some time with sulphur, they unite in the decomposed state, with considerable quantities of that substance, forming a brown, greasy, stinking mass, called *Volatile Balsam of Sulphur*, which, if heated for a longer time, quickly evolves a large quantity of sulphuretted hydrogen gas. Most camphors may also be made to unite with sulphur and phosphorus by fusion.

*γ.* Many volatile oils and camphors absorb large quantities of *hydrochloric acid gas*, producing great rise of temperature, and forming sometimes oily, sometimes camphoroïdal compounds, in which the chlorine cannot be detected by nitrate of silver. With *hydrobromic acid gas* they behave in a similar manner. Many of them combine with *chloride of phosphorus* and *chloride of sulphur*, the combination being attended with evolution of heat. They likewise absorb small quantities of carbonic oxide, carbonic anhydride, and nitrous oxide and larger quantities of sulphurous anhydride, sulphydric acid and fluoride of calcium.

*δ.* Volatile oils mix readily with *hydrocyanic acid*, abstract that acid from water, and form a mixture which does not readily decompose, and is especially heavier than water (Ittner). They absorb a few volumes of *cyanogen gas*, and dissolve *iodide of cyanogen* with facility.

*ε.* Many volatile oils and camphors are capable of mixing with certain *organic acids* such as acetic, succinic, benzoic camphoric, suberic acid, and the fatty acids. Strong acetic acid dissolves many volatile oils and camphors (Fourcroy and Vauquelin, Scher. J. v. 282; Vauquelin, Ann. Chim. Phys. xix. 279). Acetic acid, which holds volatile oils in solution, reduces mercurous nitrate or silver nitrate at a boiling heat, but not so quickly as formic acid. (Walcker.)

*ζ.* Only a few oils, which contain oxygen, and have a slightly acid character, viz. creosote, oil of cloves, and oil of pimento, absorb *ammoniacal* gas in abundance, dissolve in *aqueous alkalis*, and form with these and other bases, saline compounds, in which the odour of the oil is destroyed.

Volatile oils dissolve *oxide of copper* at ordinary temperatures, but reduce it on application of heat (A. Vogel); they dissolve *protoxide of lead* with facility (Schweitzer); mix with *chloride* and *fluoride of arsenic;* and abstract *corrosive sublimate* from its aqueous solution, whereby they become thick and solid. They also separate *chloride of gold* from its aqueous solution; and on subsequent exposure to light, the gold is set free in the metallic state.

*Adulterations of Volatile Oils.*—The more expensive of these oils are often adulterated with cheaper oils of the same class, also with fixed oils and with alcohol.

I. *With Fixed Oils.*—1. Oils thus adulterated leave upon paper a greasy spot. which remains even after long-continued warming at 100°.—2. When the mixture is distilled with *water*, the volatile oil passes over, while the fixed oil remains, and may be detected by saponifying it with potash.—3. On dissolving the volatile oil in three times its volume of 80 per cent. *alcohol*, the greater part of the fixed oil remains undissolved.

II. *With Alcohol.*—1. When the proportion of alcohol is large, the greater part of it may be extracted by *water*, the liquid acquiring a milky turbidity. Hence the quantity of alcohol may be determined by shaking up the oil with an equal bulk of water in a graduated test-tube, and observing the diminution of volume (Lipowitz). The result, however, is not quite accurate, because the separated oil still retains a portion of alcohol.—2. The mixture, when distilled with *water*, gives off the alcohol at the very beginning of the distillation; and this first distillate, when concentrated by rectification yields alcohol, easily recognised by its smell, taste, density, boiling point, and flame.—3. Into a graduated tube, two-thirds filled with the oil, some pieces of *chloride of calcium*, free from dust, are introduced, and the whole heated for five minutes on the water-bath, with frequent agitation. If no alcohol is present, the lumps of chloride of calcium appear unaltered after cooling; if a small quantity is present, they appear effloresced and baked together; and a larger quantity causes them to deliquesce with the alcohol into a fluid layer, the oil floating on the top, and appearing diminished in volume in proportion to the quantity of alcohol present.—4. *Potassium* oxidises in the alcoholised oil, with evolution of gas; and the more quickly as the proportion of alcohol is greater. Twelve drops of the oil are poured into a watch-glass, and a piece of potassium as large as a pin's head is introduced. If the potassium remains unaltered for 12 to 15 minutes, the oil is pure, or at least does not contain more than 4 per cent. alcohol; if it disappears in less than a minute, the oil contains 25 per cent. alcohol or more.—5. A pure volatile oil agitated with an equal volume of *olive-oil* yields a clear mixture; whereas that which contains alcohol forms a turbid mixture the alcohol being separated. (Righini, J. chim. méd. xx. 351.)

III. *Adulterations of expensive Oils with Oil of Turpentine.*—1. The presence of this adulteration may be detected by the smell, especially on rubbing the oil between the hands, or after setting it on fire and then blowing it out.—2. Since oil of turpentine is less soluble in hydrated alcohol than many other oils, the suspected oil may be agitated with its own bulk of 80 per cent. *alcohol;* if oil of turpentine, anise, or fennel be present, the solution is incomplete.—3. Oil of turpentine mixes much less easily with *fixed oils*, than the oils of marjoram, lavender, valerian, sage, peppermint, or wormwood. If, therefore, 3 grms. of the suspected oil be agitated with 3 grms. of *poppy oil*, and the mixture remains turbid, we may conclude that the oil is not mixed with turpentine; for even a small quantity of the latter would render the mixture clear. This method is not applicable to the oils of thyme and rosemary (Mero, J. chim. méd. xxi. 93).—4. Many volatile oils dissolve the colouring matter of *sandal-wood*, but oil of turpentine does not; the presence of the latter will, therefore, diminish the solvent power of the other oil (Voget, Ann. Pharm. vi. 42).—5. Oil of turpentine becomes strongly heated and detonates by contact with *iodine;* many other oils do not; but if the latter are mixed with only a small quantity of oil of turpentine, they likewise detonate by contact with iodine. (Tuchen.)

**OISANITE.** An old name for Anatase, from Oisans in Dauphiny.

**OKENITE.** *Dysclazite.*—A hydrated silicate of calcium, occurring in the Faroë Islands, Iceland, and Greenland, sometimes in prismatic crystals, probably trimetric and having the angle ∞P : ∞P = 122° 19′, but more generally massive and fibrous. Hardness = 4·5 to 5. Specific gravity = 2·362 (Connell); 2·28 (Kobell). White, with a shade of yellow or blue, and a pearly lustre. Often opalescent, subtransparent to subtranslucent. Very tough. Analysis 1 is by v. Hauer; 2 by Kobell (*Rammelsberg's Mineralchemie*, p. 504):

| | $SiO^2$. | $Fe^4O^3$. | $Ca^2O$. | $Na^2O$. | $K^2O$. | $H^2O$. |
|---|---|---|---|---|---|---|
| 1. Discoe Island, Greenland | 54·81 | . . | 27·23 | . . | . . | 18·04 = 100·08 |
| 2. Faroë . . . . | 57·69 | 0·54 | 26·83 | 0·44 | 0·23 | 14·71 = 100·44 |

These analyses lead to the formula $Ca^2O.2SiO^2.2H^2O$ or perhaps $Cca''H^2Si^2O^6.H^2O$, which is that of a hydrated metasilicate.

**OLEAMIDE.** $C^{18}H^{35}NO = N.H^2.C^{18}H^{33}O$.—Produced by the action of alcoholic ammonia on oil of almonds (Rowney, Ed. Phil. Trans. xxi. pt. 2; Chem. Soc. Qu. J. vii. 200), or oil of hazel-nuts (Carlet, Bull. Soc. Chim. 1859, p. 73), and purified by pressure and recrystallisation from alcohol. It forms crystalline nodules; begins to melt at 79°, becomes perfectly fluid at 81°, and solidifies to a semi-transparent mass at 78° (Rowney); at 75° to a highly crystalline mass (Carlet). It is insoluble in

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*water*, but dissolves easily in warm *alcohol;* becomes yellow and rancid when exposed to the *air;* and is decomposed by heating in a sealed tube with *alcoholic potash*, yielding oleate of potassium (Carlet). It is also decomposed by fusion with hydrate of potassium, not by boiling with aqueous potash. (Rowney.)

The conversion of oils and fats into amides by the action of ammonia was first noticed in 1844 by Boullny (J. Pharm. v. 329), who however did not obtain them pure, and regarded the products obtained from different oils as one and the same amide, which he called *margaramide*.

ELAÏDAMIDE, isomeric with oleamide, is obtained by enclosing 1 vol. elaïdin (prepared from almond-oil with nitrous acid) with 4 vol. aqueous ammonia and 2 vol. alcohol. It forms colourless shining needles which melt partially at 92°, and completely at 94°, the liquid solidifying to an opaque mass at 91°. (Rowney.)

**OLEENE.** Syn. with NONYLENE.

**OLEFIANT GAS.** Syn. with ETHYLENE.

**OLEFINES.** Hydrocarbons, $C^nH^{2n}$, homologous with ethylene; so called from their property of forming oily compounds with bromine and chlorine, like Dutch liquid (see HYDROCARBONS, iii. 187).

**OLEIC ACID.** $C^{18}H^{34}O^2 = \left.\begin{matrix}C^{18}H^{33}O\\ H\end{matrix}\right\}O.$ Chevreul, *Recherches sur les corps gras*, p. 205.—Varrentrapp, Ann. Ch. Pharm. xxxv. 196.—Gusserow, Kastner's Archiv. f. Chem. u. Meteorol. i. 73.—Laurent, Ann. Ch. Phys. lxv. 149.—Gottlieb, Ann. Ch. Pharm. lvii. 40.—Heintz, Pogg. Ann. lxxxiii. 555; lxxxix. 583; xc. 143.—Berthelot, Ann. Ch. Phys. [3] xli. 243.—The liquid acid obtained by the saponification of non-drying oils and solid fats. Under the influence of nitrous acid, it is transformed into a solid modification called *elaïdic acid*.

*Preparation.* In the manufacture of stearin-candles, oleic acid is obtained by treating with dilute sulphuric acid the lime-soap obtained by the action of lime upon tallow. The fatty acids resulting from the decomposition are washed with hot water, and solidify in mass on cooling; and this mass when subjected to pressure, yields a liquid rich in oleic acid, but still retaining a considerable quantity of stearic acid. After remaining for some time in a cold place, it deposits a quantity of solid matter, and the liquid decanted from this is sent into the market as *oleic acid*. It is an impure acid containing, besides stearic acid, a certain quantity of oxy-oleic acid produced by the oxidising action of the air.

To obtain pure oleic acid, olive or almond oil is saponified with potash; the soap is decomposed by tartaric acid; and the separated fatty acid, after being washed, is heated for some hours in the water-bath, with half its weight of oxide of lead previously reduced to fine powder. The mixture is then well shaken up with about twice its bulk of ether, which dissolves the oleate of lead and leaves the stearate; the liquid after standing for some time is decanted and mixed with hydrochloric acid; the oleic acid thereby eliminated dissolves in the ether, and the ethereal solution which rises to the surface of the water is decanted, mixed with water, and freed from ether by distillation. The residue is nearly pure oleic acid, containing only a small quantity of oxy-oleic acid. To free it from this it is saturated with ammonia, and the resulting soap is decomposed by chloride of barium, whereby a precipitate of oleate and oxy-oleate of barium is formed, which after drying is treated with boiling alcohol. The solution on cooling deposits crystals of oleate of barium, the oxy-oleate remaining in solution; and from these crystals the oleic acid may be separated in the pure state by means of tartaric acid dissolved in water which has been previously freed from air by boiling, the decomposition and the subsequent washing being carried on in such a manner as to protect the oleic acid from the action of the air.

The mode of purification just described may be applied to commercial oleic acid.

*Properties.*—Oleic acid crystallises from alcoholic solution in dazzling white needles, and melts at 14° to a colourless oil, which solidifies at 4° to a hard, white, crystalline mass, expanding at the same time to such an extent that the remaining liquid is extended (Gottlieb). Specific gravity = 0·808 at 19° (Chevreul). The acid volatilises in vacuo without decomposition (Chevreul, Laurent). It is tasteless and inodorous, reacts neutral when unaltered (not oxidised), also in alcoholic solution (Gottlieb). It contains, according to the mean of Gottlieb's analyses, 76·34 per cent. carbon, and 12·14 hydrogen, the formula $C^{18}H^{34}O^2$ requiring 76·59 C, 12·06 H, and 11·35 O.

Oleic acid is insoluble in *water*, very soluble in *alcohol*, and dissolves in all proportions in *ether*. Cold strong *sulphuric acid* dissolves it without decomposition. It dissolves solid *fats*, stearic acid, palmitic acid, &c. (Chevreul), and is dissolved by *bile*, with formation of a soap, and strong acid reaction. (Marcet, Phil. Mag. [3] xvii. 145.)

*Decompositions.*—In the solid state oleic acid oxidises but slowly in the air; but in the liquid state it rapidly absorbs oxygen, acquires a rancid taste and smell, and a decided acid reaction, no longer crystallises at low temperatures, and forms with baryta a salt very soluble in alcohol. At 100° it absorbs oxygen more rapidly than at ordinary temperatures, and gives off carbonic anhydride. (Gottlieb.)

2. Oleic acid is decomposed by distillation, yielding sebacic acid, the proportion of which is greater as the oleic acid is more nearly pure; the other products of the decomposition are caprylic, caproic, and acetic acids, several gaseous hydrocarbons, and carbonic anhydride. The formation of sebacic acid by distillation serves to distinguish oleic acid from other oily acids. (Varrentrapp)

3. Oleic acid heated with *hydrate of potassium* gives off hydrogen, and forms palmitate and acetate of potassium (Varrentrapp):

$$C^{18}H^{34}O^2 + 2KHO = C^{16}H^{31}KO^2 + C^2H^3KO^2 + H^2.$$

4. Distilled with one-fourth its weight of *quicklime*, it yields a neutral unsaponifiable liquid, probably oleone (Bussy, Ann. Ch. Pharm. ix. 271). When 10 pts. of crude oleic acid are mixed with 3 pts. of slaked lime, then with 3 pts. soda-lime, the mass distilled, and the distillate collected in a cooled receiver, liquid products are obtained, amounting to two-thirds of the oleic acid, and gases are given off consisting chiefly of ethylene, tetrylene, amylene, and olefines of higher atomic weight. (Berthelot, Ann. Ch. Phys. [3] liii. 200.)

5. Oleic acid distilled with *sulphur* gives off sulphydric acid, and yields a red-brown stinking oil, called by Anderson *sulphide of odmyl*, but perhaps consisting mainly of tetrylic mercaptan (p. 173).

6. *Chlorine* and *bromine* in presence of water, convert oleic acid into dichloroleic and dibromoleic acids respectively: iodine excites no action upon it (Lefort). Bromine added drop by drop to pure crystallised oleic acid, forms tribromo-dioleic acid. (Burg, p. 194.)

7. Strong *sulphuric acid* dissolves oleic acid, forming a solution which is precipitated by water: on heating the liquid, it blackens and gives off sulphurous anhydride. (Gottlieb.)

8. *Nitrous acid* converts oleic acid into elaïdic acid, a solid body isomeric with it.

9. Strong *nitric acid* attacks oleic acid with violence, giving off red nitrous vapours, and producing volatile acids of the series $C^nH^{2n}O^2$, viz. acetic, propionic, butyric, valeric, caproic, œnanthylic, caprylic, pelargonic, and capric acids; and fixed acids of the series $C^nH^{2n-4}O^2$, viz. suberic, pimelic, adipic, lipic, and azelaic acids, the number and proportion of these products varying with the duration of the action.

Oleic acid heated with an equal weight of *glycerin* yields triolein; with excess of glycerin, monolein. Heated with glycerin, and hydrochloric, tartaric, phosphoric, or sulphuric acid, it yields oleins containing also the radicle of the second acid, (Berthelot.)

Oleates. The formula of the neutral oleates is $C^{18}H^{33}MO^2$ or $C^{36}H^{66}M''O^4$, according to the atomicity of the metal: there are likewise acid oleates. The neutral oleates of the alkali-metals are soluble in water, and not so completely precipitated from their solutions by the addition of another soluble salt, as the stearates and palmitates. The acid oleates are liquid and insoluble in water.

The oleates dissolve in cold absolute alcohol and in ether, a property by which they may be distinguished and separated from the stearates and palmitates.

It is somewhat difficult to prepare the oleates in a state of purity, in consequence of the rapidity with which oleic acid oxidises in contact with the air. The best mode of proceeding is to decompose oleate of barium with the sulphate of the base which is to be combined with the oleic acid. The two salts are pounded together, and digested in a closed flask at a gentle heat with alcohol of specific gravity 0·833. Sulphate of barium is then formed, and the oleate of the other base dissolves in the alcohol, from which it may be freed by distillation in a current of hydrogen.

*Oleate of Ammonium* is gelatinous and soluble in water. It may be produced by digesting oleic acid in the cold with aqueous ammonia.

*Oleate of Barium*, $C^{18}H^{33}BaO^2$ or $C^{36}H^{66}Bba''O^4$, the preparation of which has already been described (p. 192), is crystalline and infusible at 100° when pure, but when altered by contact with the air, it melts below 100°.

It dissolves in warm dilute alcohol, and the solution on cooling deposits flocks consisting, according to Gössmann (Ann. Ch. Pharm. lxxxvi. 322), of an acid salt $C^{36}H^{67}BaO^4$ or $C^{36}H^{66}Bba''O^4.2C^{18}H^{34}O^2$.

The oleates of *calcium* and *strontium* closely resemble the neutral barium salt.

*Oleate of Chromium* is amorphous and violet coloured.—*Oleate of cobalt* is bluish and pulverulent.—*Oleate of copper* is a green precipitate extremely fusible, perfectly fluid at 100°.

*Oleate of Cobalt.* Oleate of potassium added to a hot solution of sulphate of cobalt, forms first a bluish-green, then a green precipitate, which settles down very slowly. (Chevreul.)

*Oleate of Copper.* By precipitating cupric sulphate with oleate of potassium or by warming oleic acid with cupric oxide, a salt of fine green colour is obtained, which becomes quite fluid at 100° (Chevreul). It dissolves in all proportions in alcohol with bluish-green colour; with a small quantity of alcohol, it forms an oil. (Unverdorben.)

*Oleates of Lead.* The *neutral salt*, $C^{18}H^{33}PbO^2$ or $C^{36}H^{66}Ppb''O^4$, is prepared by dissolving oleic acid in absolute alcohol, adding an excess of dry carbonate of sodium and heating gently, so that the vapour of the alcohol may expel the air from the flask. As soon as the liquid exhibits an alkaline reaction, it must be rapidly filtered, slightly diluted with water, and left to cool with the vessel covered; then precipitated with neutral acetate of lead, again quickly filtered, and the precipitate of oleate of lead washed in a cool place. After drying in a vacuum, it forms a light white powder, which melts at 80° to a yellow liquid. It dissolves very slowly in cold ether, but quickly in boiling ether if well stirred. It is likewise soluble in oil of turpentine and in rock-oil, the solution saturated while hot solidifying in a gelatinous mass on cooling.—When altered by contact with the air, it becomes gelatinous. (Gottlieb.)

A *basic* oleate of lead, $C^{36}H^{66}Ppb''O^4.Ppb''O$, is obtained by boiling oleic acid with excess of basic acetate of lead. It is soft at 20° and liquid at 100°. (Chevreul.)

*Oleate of Magnesium*, $C^{18}H^{33}MgO^2$ or $C^{36}H^{66}Mmg''O^4$, is granular, soft and diaphanous. (Chevreul.)

*Oleates of Mercury.* The mercuric salt is precipitated in white flocks, which become greasy when washed, and dry up to a solid mass; it dissolves sparingly in cold alcohol, more easily in hot alcohol and in ether (Harff, N. Br. Arch. v. 306).—The *mercurous salt*, $C^{18}H^{33}Hhg'O^2$, forms greyish-white flocks, becoming bluish when dry. Insoluble in water and in cold alcohol, soluble in hot alcohol, and in ether whether hot or cold. Forms with ammonia a black powder containing ammonia. (Harff.)

*Oleate of Nickel* is a greenish-yellow precipitate which settles down slowly. (Chevreul.)

*Oleates of Potassium.* The *neutral salt*, $C^{18}H^{33}KO^2$, obtained by heating equal parts of potash and oleic acid with a small quantity of water, forms a gelatinous mass which may be purified by dissolving it in alcohol. The solution evaporated to dryness leaves a white friable odourless salt, which deliquesces in moist air, dissolves completely in 4 pts. of water, forming a viscid liquid; a larger quantity of water decomposes it, separating a gelatinous mass of the acid salt. It is decomposed by acids, even by carbonic acid, when a stream of the latter is passed through the aqueous solution cooled to 5°. *Acid oleate of potassium* is insoluble in water, but soluble in alcohol even in the cold; the solution has an acid reaction.

*Oleate of Silver.* Produced by double decomposition, but reduces almost as soon as formed.

*Oleate of Sodium*, $C^{18}H^{33}NaO^2$, is obtained like the neutral potassium-salt. According to Varrentrapp, it crystallises when its solution in boiling absolute alcohol is left at rest. It dissolves in 10 or 12 parts of water, but is not deliquescent. By contact with the air it becomes gelatinous.

*Oleate of Zinc.* White powder melting below 100°. (Chevreul.)

### *Chlorine- and Bromine-derivatives of Oleic acid.*

1. *Dichloroleic acid*, $C^{18}H^{32}Cl^2O^2$.—Obtained by the action of chlorine on oleic acid in presence of water. Brown oil of specific gravity 1·082 at 8°, more viscid than oleic acid. Reddens litmus. Boils at 190°. (Lefort, J. Pharm. [3] xxiv. 113.)

2. *Dibromoleic acid*, $C^{18}H^{32}Br^2O^2$.—Obtained in like manner. Brown oil of specific gravity 1·272 at 7·5°. Reddens litmus. Boils at 200°. (Lefort.)

3. *Tribromo-dioleic acid*, $C^{36}H^{63}Br^3O^4$. Produced by adding bromine drop by drop to pure crystallised oleic acid. Viscid liquid having an agreeable odour, soluble in alcohol and ether, decomposible at 170°. It is monobasic and forms uncrystallisable salts. The *barium-salt* is a pitchy mass soluble in ether, insoluble in alcohol. The acid treated with moist silver-oxide yields oxy-oleic acid, in the form of a viscid liquid having a rancid odour and solidifying after some time. It is monobasic, and forms a gummy, deliquescent barium-salt. (Burg, J. pr. Chem. xciii. 227.)

*Acids related to Oleic acid.*

α. Hydroleic and Metoleic Acids.—When sulpholeic acid (produced by the action of sulphuric acid upon olein at low temperatures) is left to itself in the cold, it yields an oily acid called by Frémy, *meta-oleic acid.* It is insoluble in water, very sparingly soluble in alcohol, very soluble in ether. It gave by analysis 75·7 per cent. carbon, and 11·9 hydrogen.

*Hydroleic acid* is obtained, according to Frémy, by boiling the sulpholeic acid after all the meta-oleic acid has been deposited. It is oily, insoluble in water, very soluble in alcohol and ether, and contains, according to Frémy, 72·9—73·3 per cent. carbon, and 11·8—11·9 hydrogen. Both these acids are decomposed by dry distillation, yielding carbonic anhydride and oily hydrocarbons homologous with ethylene, viz. hexylene and nonylene.—(Frémy, Ann. Ch. Phys. lxv. 128). The composition, and indeed the existence of these acids, is very doubtful.

β. Elaïdic Acid, the solid fatty acid isomeric with oleic acid, produced by the action of nitrous acid on the latter, and Linoleic Acid, the fatty acid of drying oils, have been already described (ii. 368; iii. 700).

**OLEIC ETHERS.** Oleate of Ethyl or *Oleic Ether*, $C^{20}H^{38}O^2 = C^{18}H^{33}(C^2H^5)O^2$.—(Laurent, Ann. Ch. Phys. xxxv. 298. Varrentrapp, Ann. Ch. Pharm. xxxv. 206.)—This ether is obtained by passing dry hydrochloric acid gas into a solution of oleic acid in about three times its volume of alcohol. Etherification takes place in a few minutes, and the ether separates from the liquid. It may also be prepared by treating oleic acid with a mixture of alcohol and sulphuric acid.

Oleic ether is a colourless liquid of specific gravity 0·87 at 18°; soluble in alcohol and decomposible by distillation. Mercuric nitrate transforms it in 24 hours into elaïdic ether (ii. 380).

Oleate of Methyl, $C^{19}H^{36}O^2 = C^{18}H^{33}(CH^3)O^2$, obtained in like manner, is an oily liquid of specific gravity 0·879 at 18°; it is converted by mercuric nitrate into elaïdate of methyl.

Oleates of Glyceryl. Oleins.—Three of these compounds have been obtained by heating oleic acid with glycerin in sealed tubes, viz.:

| | | | |
|---|---|---|---|
| Monolein . . . . | $C^{21}H^{40}O^4$ | = | $\left.\begin{matrix}(C^3H^5)'''\\ H^2.C^{18}H^{33}O\end{matrix}\right\}O^3$ |
| Diolein . . . . . | $C^{39}H^{72}O^5$ | = | $\left.\begin{matrix}(C^3H^5)'''\\ H.(C^{18}H^{33}O)^2\end{matrix}\right\}O^3$ |
| Triolein . . . . | $C^{57}H^{104}O^6$ | = | $\left.\begin{matrix}(C^3H^5)'''\\ (C^{18}H^{33}O)^3\end{matrix}\right\}O^2$ |

They result, like other glycerides, from the union of the acid and glycerin, with elimination of the elements of water.

*Monolein*, $C^{21}H^{40}O^4 = C^{18}H^{34}O^2 + C^3H^8O^3 - H^2O$, is an oily liquid which solidifies at about 15°. Specific gravity 4·947. (Analysis 71·4 per cent. C and 11·55 H; calc. 70·8 C and 11·3 H).—It is very slowly saponified by oxide of lead. Alcohol and acetic acid do not decompose it at 100°, a property which it shares with natural olein. In the barometric vacuum it volatilises without decomposition.

It may be produced by heating glycerin and pure oleic acid to 200° in a sealed tube for 18 hours, or a mixture of oleate of ethyl, glycerin, and hydrochloric acid to 100°.

*Diolein*, $C^{39}H^{72}O^5 = 2C^{18}H^{34}O^2 + C^3H^8O^3 - 2H^2O$, is obtained by heating natural olein (triolein) with glycerin to 100° for 22 hours.—Its specific gravity is 8·921 at 21°. It begins to crystallise at about 15°. It gave by analysis 73·5 per cent. C and 11·95 H (calc. 76·2 C and 12·1 H, from the formula $C^{39}H^{74}O^6$).*

*Triolein*, $C^{57}H^{104}O^6 = 3C^{18}H^{34}O^2 + C^3H^8O^3 - 3H^2O$, is obtained by heating to 200° a mixture of equal weights of oleic acid and glycerin, decanting the layer of fatty matter after the reaction is finished, mixing it with 15 to 20 times its weight of oleic acid, and heating again to 240° for four hours. The neutral matter is extracted with lime and ether, the solution is treated with animal charcoal, then concentrated and mixed with 8 or 10 times its volume of common alcohol, and the triolein thereby precipitated is collected on a filter and dried in vacuo.

Triolein is liquid at 100°. In contact with the air, it gradually turns acid. It is slowly saponified by oxide of lead. Analysis 77·6—77·2 per cent. C and 12·2—11·5 H; calc. 77·4 C and 11·8 H.

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* The formulæ originally assigned by Berthelot to some of the glycerides containing 2 at. of the acid radicle, were founded on the supposition that the formation of these diacid compounds was attended with the elimination of only one 1 at. $H^2O$; but as such a mode of formation is not consistent with that of the other glycerides, or indeed of compound ethers in general, and as moreover it is very difficult to obtain the diacid glycerides pure, it is more probable that in the formation of these diacid glycerides 2 at. $H^2O$ are eliminated.

The olein of animal fats and non-drying oils (drying oils contain a different glyceride) appears to be identical with triolein. Its composition has not, however, been exactly determined, for there is great difficulty in obtaining it pure.

Chevreul prepared it by boiling human fat, hog's-lard, goose-fat, or beef or mutton suet in a flask, filtering the solution after leaving it to stand for 24 hours, concentrating a little by evaporation, adding water which separates the olein, then exposing the product to cold, and separating the liquid from the solid portion by pressure. In this manner olein is obtained which does not solidify at 0° C.

Olein may also be prepared from olive oil and other glycerides containing it, by pouring upon the fat a cold strong solution of caustic soda, which saponifies the stearin and the other solid fats, but not the olein. The mixture is agitated and gently heated to separate the olein from the stearin soap; the liquid is filtered through cloth, and the olein separated by decantation from the alkaline-ley. This process succeeds with all oils, excepting those which have become rancid, or have been altered by heat. (Péclet, Ann. Ch. Phys. xxii. 330.)

A less pure product is obtained by treating oil of olive or sweet almonds with cold alcohol, and evaporating the solution.

The properties of olein differ somewhat according to the nature of the fat from which it is extracted, and the mode of preparation, but when properly prepared, it is colourless, void of taste and smell, insoluble in water, very soluble in absolute alcohol and in ether, and of a density between 0·90 and 0·92. It burns with a very bright flame. When saponified with *potash*, it yields glycerin and oleate of potassium.

By *dry distillation* it yields gaseous products, liquid hydrocarbons, sebacic acid, and acrolein. This reaction affords the means of detecting olein in fats; for, if the product of the distillation be treated with boiling water, a solution is obtained which on cooling yields small needles of sebacic acid. Olein oxidises in the *air*, yielding the same products as oleic acid. Under the influence of strong *sulphuric acid*, it is resolved into sulpholeic and sulphoglyceric acids. *Nitrous acid* converts it into the isomeric solid compound elaïdin (ii. 380); this property distinguishes olein from the liquid fat of non-drying oils.

*Chlorine* and *bromine* act upon olein, producing substitution-products.

OLEATE OF MANNITYL. *Mannite oléique*, $C^{42}H^{78}O^7 = \left.\begin{matrix}(C^6H^8)^{vi}\\(C^{18}H^{33}O)^2\\H^2\end{matrix}\right\}O^6$. (Berthelot, Ann. Ch. Phys. [3] xlvii. 326).—Obtained by heating oleic acid with mannite to 120° in a sealed tube, saturating the superficial fatty layer with lime, exhausting with ether (which also takes up calcic oleate, but deposits it on boiling in vacuo) and evaporating. It is a nearly colourless, neutral, waxy mass which becomes soft and tenacious at a gentle heat and then melts to a yellowish liquid. By heating with potash it is resolved into oleic acid and mannitan.

**OLEIN.** See OLEIC ETHERS.

**OLEONE.** Oleic acid distilled with lime yields an oily liquid regarded by Bussy (p. 193) as the acetone of oleic acid; it has not, however, been obtained pure. Vohl (Dingl. pol. J. cxlvii. 304) applies the name oleone to an illuminating material of similar nature obtained by precipitating the waste-liquor of soap-works with chloride of calcium, and distilling the resulting calcium-salts of fatty acids with quicklime.

**OLEOPHOSPHORIC ACID.** A phosphoretted fatty acid contained in the brain.—When the ethereal extract of brain, prepared as described under CEREBRIN (i. 830), is treated with ether to separate cerebrin, the ether takes up oleophosphoric acid, often combined with soda, and mixed with olein and cholesterin. The ethereal solution is evaporated; the soda is extracted by an acid; the residue is dissolved in boiling alcohol; and the solution is left to cool, the oleophosphoric acid being then deposited. The olein and cholesterin still mixed with it may be removed, though not completely, by absolute alcohol. Oleophosphoric acid thus obtained is gummy, generally yellow, and contains from 1·9 to 2·0 per cent. phosphorus. When burnt in contact with the air, it leaves a carbonaceous mass containing phosphoric acid. By long boiling with water or alcohol, more quickly with acidulated water, it gradually loses its viscosity, and is converted into perfectly pure olein, while the lower stratum of liquid is rendered strongly acid by the phosphoric acid produced. The same decomposition takes place very slowly at ordinary temperatures; also at the commencement of putrefaction of the brain. Fuming nitric acid decomposes oleophosphoric acid into phosphoric acid and a fatty acid. Alkalis in excess form a phosphate, an oleate, and glycerin. The acid is insoluble in water, but swells up slightly in boiling water. With ammonia, potash, and soda, it immediately forms soapy compounds; with the other bases, insoluble salts. It is insoluble in cold absolute alcohol, easily soluble in boiling alcohol and in ether (Frémy, Ann. Ch. Phys. [3] ii. 474). The muscles of vertebrate animals, shaken up with cold weak alcohol, yield to that liquid a viscid, ambergris-coloured substance, which dissolves but imperfectly in water, and when treated with sulphuric acid, is resolved into sulphate of sodium and oleophosphoric acid. Oleophosphate of sodium occurs in almost all parts of the animal body, its quantity increasing with the age of the animal, and differing in amount in different species of vertebrate animals. Fishes with white light flesh (such as the whiting, sole, and plaice) contain but small quantities of it, whereas larger quantities are found in the herring, salmon, mackerel, salmon trout, and other fishes with firm flesh. (Valenciennes and Frémy, Ann. Ch. Phys. [3] l. 172.)

The yolk of the eggs of cartilaginous fishes contains a fat which is soluble in alcohol and ether, forms a gum with water, and resembles oleophosphoric acid. Phosphoretted fats are also found both in the slightly developed and in the ripe eggs of cartilaginous fishes. (Valenciennes and Frémy.)

**OLEUM ANIMALE DIPPELII.** See Bone-oil (i. 625) and Dippel's Oil (ii. 336).

**OLEUM JECORIS ASELLI.** *Cod-liver oil. Huile de foie de morue. Leberthran Stockfisch-thran.*—This oil is obtained from the livers of various species of *Gadus*. The oil recognised by the London pharmacopœia is that obtained from the common cod (*Gadus Morrhua*, formerly called *Asellus major*), and the ling (*G. Molva* or *Lota Molva*): it is received from Newfoundland. England was formerly supplied with the oil from Bergen, obtained from the livers of the dorse (*Gadus cellarius*) and coal-fish (*G. carbonarius*). From this source Germany and the North of Europe still receive their supply. Cod-liver oil is prepared on a small scale in the Shetland isles and on the English coast, chiefly from the common cod, the ling and the burbot (*Lota vulgaris*). (*Pereira's Materia Medica*, 4th ed. 1857, ii. [2] 779.)

When the livers of the fishes are exposed to the sun, light-coloured oil flows out at first, but after a week or a fortnight, putrefaction sets in and brown oil is obtained. (Marder.)

*a. Brown Cod-liver oil.* Dark brown, greenish by transmitted light, transparent in thin layers. Specific gravity 0·929 at 17·5° (De Jongh), 0·928 at 15·5° (Marder); has a peculiar odour, disagreeably empyreumatic and bitter, produces irritation in the throat, and reddens litmus slightly (De Jongh). Does not deposit any solid fat at −13° (Marder). Soluble in 17 to 20 pts. cold or hot absolute alcohol (De Jongh). Dissolves at 71° in 1 pt. alcohol of 0·846, forming a solution which becomes turbid at 62° and deposits the oil at 48°. (Marder.)

*b. Paler brown.* Of the colour of Malaga wine. Specific gravity 0·924; has a peculiar, not unpleasant odour, fishy taste, producing irritation in the throat, and reddens litmus strongly. Soluble in 31 to 36 pts. of cold and 13 pts. of boiling absolute alcohol. (De Jongh.)

*c. Paler and clearer.* Of golden yellow colour: specific gravity 0·923 at 17·5° (De Jongh), 0·928 at 15·5 (Marder), reacts and tastes like *b*, but less strongly. Deposits a white fat at − 13° (Marder). Soluble in 40 pts. cold and in 22 to 30 pts. boiling absolute alcohol (De Jongh). Oil of haddock's liver has a specific gravity of 0·9313 at 11°. (Scharling.)

Cod-liver oil consists chiefly of olein and margarin, with smaller quantities of free butyric acid, acetic acid, constituents of the bile, gaduin, and other peculiar substances, about 1 per cent. of salts, and a small quantity of free phosphorus (De Jongh). It contains iodine, bromine, and sulphur. As volatile acids, Wagner found butyric and capric acids; from turbid cod-liver oil Luck's gadinic acid (ii. 756) was deposited. See analyses of cod-liver oil by Marder (N. Br. Arch. xiii. 153); De Jongh (Ann. Pharm. xlviii. 362); Riegel (N. Br. Arch. lxx. 23); for Winckler's views respecting the oil, see J. pr. Pharm. xxv. 140.

When a mixture of cod-liver oil and strong sulphuric acid is heated with an alkali, a pungent odour is evolved, like that of oil of rue; and on distilling the mixture with water, a small quantity of yellowish oil is collected, having the same odour, lighter than water, and boiling at 100°.

Cod-liver oil treated with alcoholic ammonia, forms a large quantity of amide, melting at 80° (Carlet). Rowney obtained a small quantity of amide melting at 93°, becoming solid and transparent at 94°, containing on the average 75·69 per cent. carbon, 12·99 hydrogen and 4·35 nitrogen, and easily soluble in alcohol.

Cod-liver oil is much used in medicine. It has long been a popular remedy for rheumatism and some other complaints, but its use by medical practitioners is of comparatively recent date. It is chiefly prescribed in cases of rheumatism, scrofula, chronic gout, skin affections, phthisis and mesenteric emaciation. Its efficacy may perhaps be due to the bromine and iodine contained in it, though it has often been doubted whether it possesses any virtues beyond those of the fat oils in general.

For further details respecting the composition, properties and uses of cod-liver oil, see De Jongh (*L'huile de foie de morue envisagée sous tous les rapports comme moyen thérapeutique*, Paris, 1853); respecting composition and properties, see also *Gmelin's Handbook* (xvi. 323).

**OLIBANUM** or *Incense.* A gum-resin which exudes from a tree, probably a species of *Balsamodendron* (order *Terebinthaceæ*), growing in Arabia and India. It has been burnt from all antiquity in religious ceremonies. It occurs in oblong or rounded laminæ, opaque, of yellow or reddish colour, dull and waxy on the fractured surface. It softens between the teeth, producing an aromatic slightly rough taste. It is but partially soluble in water and alcohol, melts with difficulty and imperfectly when heated, and burns with a bright white flame on the approach of a taper. According to Braconnot (Ann. Ch. Phys. [2] lviii. 60) it contains 56 per cent. resin soluble in alcohol, 30·8 gum soluble in water; 5·2 residue insoluble in water and in alcohol, and 8·0 essential oil and loss. Hekmejer (Jahresb. 1858, p. 482) found in olibanum a gum which appeared to be identical with gum-arabic. According to Johnston (*loc. cit.*) commercial olibanum consists chiefly of an acid resin containing, on the average, 7·4 per cent. carbon and 9·98 hydrogen, agreeing nearly with the formula $C^{20}H^{30}O^{2}$.

Stenhouse (Ann. Ch. Pharm. xxxv. 306), by distilling olibanum with water, obtained 4 per cent. of colourless volatile oil, of specific gravity 0·866 at 20°, having an odour like that of oil of turpentine, but more agreeable; insoluble in aqueous alcohol, but soluble in all proportions in ether and absolute alcohol, and containing 83·83 per cent. C, 11·27 H, and 4·90 O.

**OLIDIC ACID.** This name was given by Varrentrapp (Ann. Ch. Pharm. xxxv. 210) to an acid obtained by the action of melting potash on oleic acid; according to Heintz, this acid is palmitic acid (p. 193).

**OLIGISTIC IRON.** Syn. with Red Hæmatite (iii. 337, 393).

**OLIGOCLASE.** *Soda-spodumene, Natron-spodumen.* A mineral of the felspar group (ii. 618) occurring in granite, porphyry, syenite, serpentine, basalt and trachyte. It forms triclinic prisms in which ∞'P : ∞P,' = about 120°; oP : ∞P̆∞ = 93° 15'; oP : ∞P' = 115° 37'. Cleavage very distinct, parallel to oP and ∞P̆∞ Twins common.

Hardness = 6. Specific gravity = 2·58 – 2·69. Lustre vitreous, vitreo-pearly or greasy. Colour, yellowish, greyish, reddish, greenish-white, or white. Transparent to subtranslucent. Fracture conchoïdal to uneven. Before the blowpipe it melts quickly and more easily than orthoclase, to a glass either clear or enamel-like. It is not acted upon by acids.

*Analyses*:—*a.* From Unionville, Pennsylvania (*Unionite*), where it occurs in granite with euphyllite and corundum: specific gravity 2·61 (Smith and Brush, Sill. Am. J. [2] xv. 211).—*b.* Reddish from old red porphyry (Delesse, Ann. Ch. Phys. [3] v. 14).—*c.* From the emerald mines of the Ural, in mica-slate: white; specific gravity 2·656 (Jewreinow, *Rammelsberg's Mineralchemie*, p. 613).—*d.* From Tvedestrand in Norway (*Sun stone*): in gneiss; specific gravity 2·656 (Scheerer, Pogg. Ann. lv. 109.—*e.* From the diabase of Chalanges, near Allemont in Dauphiny: milk-white (Lory, Bull. géolog. [2] vii. 642).—*f.* From Piz Rosag in the Grisons; with hornblende in diorite. Massive; specific gravity 2·835 (v. Rath, Zeitschr. d. geolog. Gesellsch. ix. 226, 259).—*g.* From the lava of Lake Laach: specific gravity 2·56. (Fouqué, Compt. rend. xix. 46).—*h.* From the trachyte of Teneriffe: specific gravity 2·58—2·59 (Deville, *loc. cit.*).—*i.* From cavities in the lava near Hafnefjord in Iceland (*Hafnefjordite, lime-oligoclase*): specific gravity 2·729 (Forchhammer, J. pr. Chem. xxx. 489).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
|---|---|---|---|---|---|---|---|---|---|
| Silica . . . . | 64·27 | 58·92 | 60·63 | 61·30 | 59·4 | 57·64 | 63·5 | 62·54 | 61·22 |
| Alumina . . . . | 21·21 | 22·49 | 26·35 | 23·77 | 24·2 | 22·99 | 22·1 | 22·49 | 23·32 |
| Ferric oxide . . . | . . | 0·75 | 0·40 | 0·36 | 0·6 | 3·92 | . . | . . | 2·40 |
| Lime . . . . | 0·81 | 6·13 | 4·15 | 4·78 | 3·7 | 8·09 | 0·3 | 2·18 | 8·82 |
| Magnesia . . . . | 0·58 | 1·87 | 0·25 | . . | . . | 0·37 | 1·8 | 0·41 | 0·36 |
| Soda . . . . | 10·94 | 6·93 | 5·60 | 8·50 | 7·0 | 5·25 | 8·9 | 7·84 | 2·56 |
| Potash . . . . | 1·36 | 0·93 | 1·17 | 1·29 | 3·4 | 1·79 | 3·4 | 4·54 | trace |
| Water . . . . | 1·08 | 1·64 | . . | . . | 1·5 | | | | |
| | 100·25 | 99·66 | 98·55 | 100·00 | 99·8 | 100·05 | 100·0 | 100·00 | 98·68 |

Most of these analyses, and numerous others that have been made of oligoclase from various localities, may be represented by the general formula $2M^2O.2Al^2O^3.9SiO^2$, in which the oxygen-ratio of the protoxides, alumina and silica is as 1 : 3 : 9 (see ii. 618). The ratio between the lime and alkalis is somewhat variable, but the soda is for the most part predominant. An isomorphous mixture containing $2(\frac{2}{3}Na.\frac{1}{3}Ca)^2O.2Al^2O^3.9SiO^2$ would contain 63·01 per cent. silica, 23·55 alumina, 4·24 lime, and 8·40 soda. In oligoclase from the Ural (*c*), and some others, the proportion of alumina appears to be considerably greater; this may arise from loss of alkalis by weathering (or it may be due to incorrect determination of the alkalis). The mineral from Hafnefjord (*i*) is remarkable for the large proportion of lime which it contains.

**OLIGON-SPAR.** Breithaupt's name for spathic iron (ferrous carbonate) from Ehrenfriedersdorf.

**OLIVE.** *Olea europæa.*—The development of fatty matter and of mannite in the fruit of this tree has been recently examined by De Luca (Compt. rend. liii. 380; lv. 470, 506; lvii. 520; Jahresb. 1861, p. 739; 1862, p. 505; 1863, p. 611). The fruit, which at first weighs only a few millegrammes, goes on increasing in weight till November, its weight when ripe being about 2 grammes; the weight of the kernel however increases only from its first development till August, after which it remains stationary. The density of the entire fruit, which in its early stages is about equal to that of water, increases to about 1·04 when the fruit has become quite green; and then diminishes as the fruit ripens, the ripest fruits having the smallest density (1·007). The proportion of water in olives decreases from 60—70 per cent. in the earliest stage of the fruit to 25 per cent. in the ripe fruit. Olives yield to sulphide of carbon a variety of substances including colouring matters, and especially chlorophyll, the quantity of which continually diminishes as the fruit ripens. The fat, which is present only in small amount in the young fruit, increases continually as the fruit grows, and attains its maximum (69·8 per cent.) in the ripe fruit which has lost all traces of green colouring. The increased development of fat begins at the time when the weight of the kernel becomes stationary. The formation of fat is accelerated by the action of air and light.

The green substance of the leaves and fruit of the olive-tree is always accompanied by mannite, which indeed is present in all parts of the tree. The leaves contain at first but a small quantity of mannite: it increases as they grow, but diminishes at flowering time, and disappears altogether as the leaves turn yellow and fall. The flowers also contain a considerable quantity of mannite; but those which fall off after impregnation contain not a trace of it. Olives when scarcely formed are rich in mannite; the proportion of this substance diminishes however as the fruit grows; and in ripe olives, no longer green, but containing the maximum of fat, it is altogether absent.

Olives, especially in the green state, contain, together with mannite, a peculiar bitter substance, easily soluble in water, less so in alcohol.

**OLIVE OIL.** This fat oil is extracted from the fleshy portion or pericarp of the fruit of the olive. Several qualities of it are found in commerce. The best, called *virgin oil*, which has an agreeable odour and is used for culinary purposes, is obtained from fresh olives by pressure. The oil of second quality, which is more apt to turn rancid than the preceding, in consequence of the mucilaginous particles with which it is mixed, is prepared from the pulp of olives from which the virgin oil has been expressed, by macerating it in boiling water, and pressing it again. This oil, called *ordinary oil* (*huile tournante*), is chiefly used for oiling goods which are to be dyed with Turkey red. A third and still inferior quality of oil, unfit for culinary purposes, is obtained either by pressing the olives a second time with water, or by the use of inferior olives. Lastly, a very crude oil called *infernal oil* (*huile d'enfer*) is obtained from the water which has been used in pressing the olives, and still contains some of the oil in suspension, by leaving it to repose in cisterns called *enfers*. The inferior kinds of olive oil are used chiefly for burning, in the manufacture of cloth, and in soap-making.

Pure olive oil has a pale yellow colour, an agreeable taste, and a very faint odour. According to Saussure, its specific gravity is 0·9192 at 12°, 0·9109 at 25°, 0·8392 at 50°, and 0·8624 at 94°, that of water at 15° being equal to unity; according to Pohl, it is 0·91635 at 17·5° compared with water at the same temperature. It boils at 315° (Saussure). The cold-prepared oil contains 77·36 per cent. carbon, 11·45 hydrogen, and 11·29 oxygen. (Lefort.)

Olive oil is resolved by saponification into glycerin and fatty acids, which, according to the older statements of Chevreul, and of Pelouze and Boudet, consists of margaric and oleic acids; according to Collett (J. pr. Chem. lxiv. 108) of palmitic and oleic acids; according to Heintz and Krug (*ibid.* lxx. 367) of oleic, palmitic, butic, and perhaps also stearic acid. According to Benecke (*Studien*, p. 108) olive oil contains cholesterin.

Olive oil solidifies at temperatures above 0° C., often at 10°, small granules separating out; by cooling and pressure it may be resolved into a permanently fluid, and a solidifiable portion called *olive-oil tallow*, or by Pelouze and Boudet, *oleo-margarin*; it melts at 22°—28°. The permanently fluid portion of olive oil consists of triolein.

Olive-oil treated with moist *chlorine* and *bromine* yields substitution products. The *chlorinated oil* is colourless, and of the consistence of castor-oil, of specific gravity 1·078 at 10°, and contains 20·47—21·01 per cent. chlorine. The *brominated* oil is of the same consistence, but has a yellowish tint: specific gravity 1·276 at 9·5°; contains 36·48—36·37 per cent. bromine. (Lefort.)

For further details on the reactions of olive oil, see *Gmelin's Handbook*, vol. xvii. under *Triolein*. Respecting the method of detecting adulterations of olive oil, see OILS, p. 181.

**OLIVENITE.** *Prismatic Arsenate of copper. Pharmacochalcite. Olivenerz.*—A cupric phosphato-arsenate, occurring, sometimes in long rhombic prisms or needles, sometimes in spherical or ovoid aggregations resembling malachite; sometimes fibrous, forming the variety called *wood-arsenate* (*Holzkupfererz*). Hardness = 3. Specific gravity = 4·1—4·4; of the wood-arsenate 3·913. Lustre adamantine to vitreous. Colour olive-green, or sometimes brown. Streak olive-green to brown. Subtransparent or opaque. Fracture, when observable, conchoïdal or uneven. Brittle.

The principal localities of the mineral are the Redruth and other mines in Cornwall; it is also found on Alston Moor in Cumberland; at Camsdorf and Saalfield in Thuringia; in the Tyrol, the Bannat, Siberia, Chile, and other places.

The following analyses are of specimens from the Cornish mines (Rammelsberg's *Mineralchemie*, p. 374):

| | *Crystallised.* | | | | *Fibrous.* |
|---|---|---|---|---|---|
| | Richardson. | Kobell. | Hermann. | Damour. | Hermann. |
| Arsenic Anhydride . . | 39·85 | 36·71 | 33·50 | 34·87 | 40·50 |
| Phosphoric Anhydride . . | . . | 3·36 | 5·96 | 3·43 | 1·00 |
| Cupric Oxide . . . | 56·42 | 56·43 | 56·38 | 56·86 | 51·03 |
| Ferrous Oxide . . . | . . | . . | . . | . . | 3·64 |
| Water . . . . | 3·73 | 3·50 | 4·16 | 3·72 | 3·83 |
| | 100·00 | 100·00 | 100 00 | 98·88 | 100·00 |

The analyses lead to the formula $4Cu^2O.(As;P)^2O^5.H^2O$ or $\overset{\prime\prime}{Cu}{}^3(As;P)^2O^8.\overset{\prime\prime}{Cu}H^2O^2$, which, if the number of atoms of arsenic be supposed to be six times as great as that of the phosphorus atoms, will give 35·70 per cent. $As^2O^5$, 3·69 $P^2O^5$, 57·40 $Cu^2O$, and 3·21 $H^2O$.

Olivenite is homœomorphous with libethenite from Hungary, $\overset{\prime\prime}{Cu}{}^3P^2O^8.\overset{\prime\prime}{Cu}H^2O^2$.

**OLIVENOÏD.** Shepard's name for a mineral resembling olivin, which he supposes to exist in certain meteorites.

**OLIVIL.** $C^{14}H^{18}O^5$. (Pelletier, Ann. Ch. Phys. [2] iii. 105; li. 196. Sobrero, J. Pharm. [3] iii. 286).—A neutral substance occurring together with resin and a little benzoic acid in the gum of the olive-tree. To obtain it, the finely powdered gum is digested with ether to remove the resin, and the residue is boiled with alcohol. The quickly-filtered solution solidifies to a crystalline mass, which is purified by washing with cold alcohol and re-crystallising from a boiling alcoholic solution. (Pelletier, Sobrero.)

Olivil separates from absolute alcohol in colourless anhydrous crystals, which are inodorous, and have a bitter-sweet, somewhat aromatic taste. At 118°—120° it melts without loss of weight to a transparent liquid, which solidifies, on cooling, to a colourless or yellowish transparent resin, which cracks, and, when powdered, becomes electric; heated to 70°, it again becomes fluid, but crystallises from alcohol in its original state. It is very soluble in *water*, especially at the boiling heat; it dissolves in all proportions in boiling *alcohol*, and in small quantity in *ether* and in *oils*.

Anhydrous olivil contains, according to the mean of Sobrero's analyses, 61·01 per cent. carbon, and 7·08 hydrogen; the formula $C^{14}H^{18}O^5$ requires 61·09 carbon, 6·9 hydrogen, and 32·01 oxygen. Olivil crystallises from water in colourless transparent prisms, containing $C^{14}H^{18}O^5.H^2O$ or 6·33 per cent. water, half of which they give off when dried in a vacuum and the whole when melted.

*Decompositions.*—Olivil subjected to *dry distillation* melts and puffs up, giving off water (acetic acid according to Pelletier) and pyrolivilic acid, whilst a black pasty mass, partially soluble in alcohol, remains behind. By prolonged heating, other volatile products, differing from pyrolivilic acid, are obtained, till at last charcoal remains (Sobrero).—2. It burns with a white flame, and leaves a large quantity of porous charcoal.—3. *Chlorine*, passed into aqueous olivil, throws down brown flakes containing chlorine, which are afterwards decomposed, with evolution of carbonic anhydride—4. Strong *sulphuric acid* colours olivil blood-red, and then carbonises it; from a moderately dilute aqueous solution of olivil it precipitates olivirutin.—5. Dry olivil absorbs *hydrochloric acid gas*, becoming transparent and green, and, on heating, is converted into olivirutin (p. 202).—6. Strong *nitric acid* attacks it violently, with abundant evolution of nitric peroxide. With nitric acid diluted with its own volume of water, it forms a deep red-yellow solution, which, when heated, becomes nearly colourless, evolving scarcely any red fumes, but much hydrocyanic acid, and contains, after the reaction, a large quantity of oxalic acid.—Very weak nitric acid colours aqueous olivil reddish-yellow.—7. A solution of olivil in *caustic potash* assumes a yellowish-green, afterwards a brown colour, more especially on exposure to the air.—8. *Chromic acid* and dichromate of potassium precipitate aqueous olivil in brown flakes, which soon become green and granulated, and appear to consist of the chromium-salt of an acid formed by the oxidation of olivil. No gas is evolved in the reaction.—9. *Peroxide of lead* is decolorised by boiling with aqueous olivil, without evolution of gas, and, after some days' boiling, is converted into a light powder containing oxide of lead and a resinous oxidation-product of olivil.—10. Aqueous olivil colours *sulphate of copper*, on boiling, pale-green; it immediately reduces *gold* and *silver-salts*. (Sobrero.)

*Lead-salt of Olivil.* On adding ammonia to a solution of nitrate of lead containing a large excess of olivil, a white precipitate is formed containing 34·4 per cent. carbon, 3·4—3·7 hydrogen, and 45·2—45·0 lead-oxide, agreeing nearly with the formula $C^{14}H^{18}O^5.Ppb''O$.

**OLIVIN.** *Chrysolite, Boltonite, Forsterite, Glinkite, Hyalosiderite, Peridote.*—A silicate of iron and magnesium $2(Mg; Fe)^2O.SiO^2$ or $(Mmg''; Ffe'')^2SiO^4$, occurring sometimes in transparent crystals (chrysolite), but more usually in imbedded masses or grains, in lava and basalt, and in many meteorites (iii. 977). The crystals are trimetric, having the ratio of the axes $a : b : c = 0·466 : 1 : 0·5867$. Angle $\infty P : \infty P = 49·58$; $\infty\breve{P}2 : \infty\breve{P}2 = 86·0°$; $\breve{P}\infty : \breve{P}\infty$ (basal) $= 60° 48'$; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) $= 99° 7'$; $\bar{P}\infty : \bar{P}\infty$ (basal) $= 103° 6'$. They are usually short prisms formed by the vertical prismatic faces above mentioned and the faces $\infty\bar{P}\infty$ and $\infty\breve{P}\infty$; the ends are bevelled with one or more of the above-mentioned domes, or terminated by the basal face oP, the latter however seldom predominating. Cleavage tolerably easy parallel to $\infty\breve{P}\infty$ (Kopp's *Krystallographie*). Hardness = 6·7. Specific gravity = 3·33—3·5. Lustre vitreous. Colour green, commonly olive-green, sometimes brownish; black in some highly ferruginous varieties; rarely white. Streak uncoloured. Transparent. Fracture conchoïdal.

Olivin rich in iron melts before the blowpipe to a black magnetic bead, but the varieties containing but little iron are infusible. Olivins are decomposed by hydrochloric acid, the iron olivins also more easily than the others. According to v. Kobell, olivin forms a jelly with sulphuric acid.

*Analyses:* a. *Forsterite* from Somma: white, crystallised; specific gravity 3·243; slowly gelatinising with silica (Rammelsberg, *Mineralchemie*, p. 437).—*b. Boltonite* from Bolton, Massachussetts: greenish-yellow; specific gravity 3·328 (Smith, Sill. Am. J. [3] xviii. 372).—*c.* Grains from the Thjorslava, Hecla: specific gravity 3·226 (Genth, Ann. Ch. Pharm. lxvi. 20).—*d. Chrysolite*, from the East (Stromeyer, Pogg. Ann. iv. 193).—*e.* From the fumarole of Mascala, Etna: crystallised; specific gravity 3·334 (v. Waltershausen, *Vulkanische Gesteine*, p. 117).—*f.* From Petschau in Bohemia, in basalt (Rammelsberg).—*g.* From the Pallas meteorite (Stromeyer, *loc. cit.*).—*h.* From the meteoric iron of Atacama (Schmid, Pogg. Ann. lxxxiv. 501).—*i.* From Tissersk in the Ural, in mica-slate; specific gravity 3·39—3·43 (Hermann, J. pr. Chem. xlvi. 222).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
|---|---|---|---|---|---|---|---|---|---|
| Silica | 42·41 | 42·31 | 43·44 | 39·73 | 41·33 | 44·67 | 38·48 | 36·92 | 40·04 |
| Magnesia | 53·30 | 51·16 | 49·31 | 50·13 | 47·44 | 41·84 | 48·42 | 43·16 | 42·60 |
| Ferrous oxide | 2·33 | 2·77 | 6·93 | 9·19 | 10·38 | 10·76 | 11·19 | 17·21 | 17·58 |
| Manganous oxide | . . | . . | . . | 0·08 | . . | . . | 0·34 | 1·81 | |
| Nickel oxide | . . | . . | 0·32 | 0·32 | 0·21 | 2·35 | . . | . . | 0·15 |
| Alumina | . . | 0·18 | . . | 0·22 | 0·64 | 0·23 | 0·18 | | |
| Loss by ignition | . . | 1·90 | | | | | | | |
| | 98·04 | 98·32 | 100·00 | 99·67 | 100·00 | 99·85 | 98·61 | 99·10 | 100·37 |

These analyses and numerous others of olivin from various localities may be represented by the general formula above given, the magnesium and iron replacing each other isomorphously. For other analyses see Rammelsberg's *Mineralchemie*, pp. 437–441; and further, Jahresb. 1861, p. 987; 1862, 727; 1863, p. 803.

*Hyalosiderite* (iii. 177) may be regarded as an olivin, $(\frac{1}{3}Ffe''.\frac{2}{3}Mmg'')^2SiO^4$, having part of the silica replaced by alumina.

*Eulysite-olivin*, from the gneiss of Tunaberg in Sweden (ii. 606), contains 29·34 per cent. silica, 3·04 magnesia, 54·71 ferrous oxide, 8·39 manganous oxide, 3·07 lime, and 1·21 alumina, and may be represented by the formula $(\frac{1}{8}Mmn.\frac{1}{12}Mmg.\frac{1}{24}Cca.\frac{3}{4}Ffe.)^2SiO^4$ or $(\frac{1}{2}Mmn.\frac{1}{3}Mmg.\frac{1}{6}Cca)^2SiO^4 + 3Ffe^2SiO^4$.

Damour (Ann. Min. [4] viii. 90) describes as titaniferous olivin a massive red-brown mineral from the mica-slate of Pfunders in the Tyrol, having a specific gravity of 3·25, and containing (mean of two analyses) 36·58 per cent. silica, 4·40 titanic anhydride, 49·89 magnesia, 6·10 ferrous oxide, 0·60 manganous oxide, and 1·73 water.

**OLIVIRUTIN.** A red substance produced by the action of sulphuric or hydrochloric acid on olivil. It is precipitated on pouring strong sulphuric acid into a concentrated solution of olivil, in red flocks, which ultimately dissolve in the acid, but are reprecipitated by water. It dissolves in ammonia with fine violet colour; also in alcohol, whence it is precipitated by water. It contains from 68·0 to 69·1 per cent. carbon, and 5·9 to 6·4 hydrogen, and according to Sobrero, differs from olivil by the elements of water. The alcoholic solution precipitates basic acetate of lead, and after addition of ammonia, likewise barium- and calcium-salts; it precipitates cupric acetate after some time.

**OLIVITE.** A bitter substance obtained by Landerer from unripe olives, by extraction with dilute hydrochloric or sulphuric acid and precipitation with water. It dissolves in alcohol, and separates, after concentration, in bitter neutral crystals, insoluble in water, but soluble in dilute acids. The same substance appears to have been obtained from the leaves of tha olive tree by a different process. (Handw. d. Chem. v. 696.—Gm. xvi. 197.)

**OMICHMYL, OXIDE OF.** A substance contained, according to Scharling (Ann. Ch. Pharm. xlii. 265), in the ethereal extract of urine (ὀμιχμα). It is of resinous consistence, melts in boiling water to a yellowish oil, and dissolves in alcohol, ether and alkalis. Chlorine converts it into a substance said to have the composition of chloride of salicyl, $C^7H^5O^2Cl$.

**OMPHAZITE.** A foliated leek-green variety of augite, having nearly the composition of diopside, but with rather more iron. Specific gravity 3·23—3·3. It accompanies granular garnet on the Sau Alp; occurs also in Carinthia and near Hof in Bayreuth, with the smaragdite variety of hornblende, which it much resembles.

**ONEGITE.** Göthite from Lake Onega.

**ONKOSIN.** An argillaceous mineral from the Salzburg Alps, occurring in roundish pieces, having an apple-green colour, sometimes greyish or brownish, with weak greasy lustre; translucent. Hardness = 2. Specific gravity = 2·8. Fracture fine-splintery. Fuses with intumescence before the blowpipe to a white blebby glass. Soluble in sulphuric, insoluble in hydrochloric acid. Contains 52·52 per cent. silica, 30·88 alumina, 3·82 ferrous oxide, 6·38 potash, and 4·60 water. (v. Kobell, J. pr. Chem. ii. 295.)

A mineral from the Ochsenkopf near Schwarzenberg, usually regarded as an agalmatolite, and found by John (Ann. Phil. iv. 214) to contain 55 per cent. silica, 30 alumina, 1 ferric oxide, 1·75 lime, 6·25 potash, and 5·5 water, belongs properly to onkosin. (Scheerer.)

**ONOCERIN.** $C^{12}H^{20}O$? (Hlasiwetz, J. pr. Chem. lxv. 142.)—A crystallisable substance contained, together with ononin, in the root of *Ononis spinosa*, and separating from the concentrated alcoholic decoction in strongly coloured crystals, which may be purified by pressure, washing with cold alcohol, and recrystallisation from boiling alcohol, with aid of animal charcoal. It forms interlaced capillary crystals, insoluble in *water*, sparingly soluble in *ether*, perfectly soluble in boiling *alcohol* and in warm *oil of turpentine;* melts to a colourless liquid, which solidifies to a crystalline mass, and is not altered by boiling with hydrochloric acid, or with potash-ley. *Chlorine* at 100°, converts it into chloronocerin, $C^{12}H^{18}Cl^2O$, a resinous substance, insoluble in water and in alcohol, easily soluble in ether.

**ONOFRITE.** Native selenio-sulphide of mercury (iii. 912).

**ONONETIN.** $C^{48}H^{44}O^{13}$. (Hlasiwetz, *loc. cit.*)—A substance produced, together with glucose, by the action of dilute acids on onospin (p. 203):

$$C^{60}H^{68}O^{25} = C^{48}H^{44}O^{13} + 2C^6H^{12}O^6;$$

also by boiling formonetin (ii. 695) with baryta-water:

$$\underset{\text{Formonetin.}}{C^{50}H^{40}O^{13}} + 4H^2O = \underset{\text{Formic acid.}}{2CH^2O^2} + \underset{\text{Ononetin.}}{C^{48}H^{44}O^{13}}$$

To prepare it, onospin is boiled with about ten times its weight of water, and sulphuric acid is added drop by drop till the solution becomes turbid. On continuing the boiling, the ononetin collects at the bottom in a fused mass which becomes crystalline on cooling, and may be purified by recrystallisation from strong alcohol.

Ononetin forms long, colourless, brittle prisms, grouped in stars or bundles, nearly insoluble in *water*, soluble in *alcohol*, slightly soluble in warm *ether*, more soluble in *alkalis*. It gives off 1·86 per cent. water at 100°, melts at 120°, and solidifies in a radiate mass on cooling; it cannot be volatilised. Its solution does not precipitate any metallic salt, except *basic acetate of lead*. It is coloured red by *strong sulphuric acid and peroxide of manganese*, deep red by *ferric chloride*. When heated with *nitric acid*, it melts like a resin, and oxidises, emitting a very irritating odour; the solution contains oxalic acid, and apparently picric and oxipicric acids. The ammoniacal solution, when exposed to the air, acquires a fine deep green colour, and hydrochloric acid then throws down from it a dark red resinous substance soluble in alcohol.

**ONONIDE.** This name was given by Reinech (Repert. Pharm. [2] xxvi. 12) to a substance resembling glycyrrhizin, which he obtained from the aqueous decoction of the root of *Ononis spinosa* by precipitation with sulphuric acid. Hlasiwetz however found the substance thus obtained to be of variable composition, and is of opinion that the root contains true glycyrrhizin, which gradually becomes altered by oxidation.

**ONONIN.** $C^{62}H^{68}O^{27}$.—A substance existing in the root of *Ononis spinosa*; discovered by Reinscb (*loc. cit.*), further investigated by Hlasiwetz (Wien. Acad. Ber. xv. 142). It is prepared by precipitating the clarified aqueous decoction of the root with a slight excess of basic acetate of lead, decomposing the precipitate with sulphydric acid, and treating the washed and dried sulphide of lead several times with boiling alcohol. The alcoholic liquors freed from alcohol by distillation, and left to evaporate, deposit the ononin in crystalline nodules, which may be freed from adhering brown resin by treatment with alcohol. (Hlasiwetz.)

Pure ononin forms colourless needles or scales, tasteless, inodorous, insoluble in cold water, sparingly soluble in boiling *water*, more soluble in boiling *alcohol*, nearly insoluble in *ether*. It melts and turns brown at 235°. Contains according to Hlasiwetz, 58·28—61·75 per cent. carbon, and 5·45—5·68 hydrogen; the formula above given requires 59·80 carbon, 5·46 hydrogen, and 34·74 oxygen.

The alcoholic solution of ononin does not precipitate any metallic salts except *basic acetate of lead*, with which it forms white flocks. It is not coloured by *ferric chloride*, or by *chlorine-water*. It is dissolved at the boiling heat by caustic *potash*, and more easily by *baryta-water*, yielding a formate and onospin:

$$\underset{\text{Ononin.}}{C^{62}H^{68}O^{27}} + 2H^2O = \underset{\text{Onospin.}}{C^{60}H^{68}O^{25}} + \underset{\text{Formic acid.}}{2CH^2O^2}$$

Strong *sulphuric acid* dissolves it, forming a reddish-yellow solution which becomes cherry-red after some time, and immediately assumes a fine crimson colour on addition of a few grains of manganic peroxide. *Hydrochloric acid* and *dilute sulphuric acid* dissolve ononin with aid of heat, yielding formonetin and glucose:

$$C^{62}H^{68}O^{27} = C^{50}H^{40}O^{13} + 2C^6H^{12}O^6 + 2H^2O.$$

Boiling *nitric acid* dissolves it, with deep yellow colour, producing oxalic acid. (Hlasiwetz.)

**ONONIS.** The root of the spinous rest-harrow (*Ononis spinosa*) contains, according to Hlasiwetz, two crystallisable substances, ononin and onocerin, a substance allied to glycyrrhizin, and citric acid, besides the constituents common to all plants.

The ash of the root was found by Bnkeisen (Jahresb. 1855, p. 717), to contain 15·76 per cent. potash, 3·78 soda, 2·09 chloride of sodium, 20·87 lime, 13·37 magnesia, 4·29 ferrous oxide with trace of manganese, 4·85 silica, 7·93 phosphoric anhydride, 8·88 sulphuric anhydride, 8·60 carbonic anhydride, with 12·60 sand and charcoal.

**ONOSPIN.** $C^{60}H^{68}O^{25}$. (Hlasiwetz, *loc. cit.*)—A substance produced, together with formic acid, by boiling ononin with baryta-water. After all the ononin is dissolved, a stream of carbonic acid gas is passed into the liquid, and the precipitate is washed with cold and digested in boiling water, which dissolves the onospin, and deposits it on cooling as a white interlaced crystalline mass. It is insoluble in *ether*, but easily soluble in *alcohol*. It dissolves also in *alkalis*, and is precipitated by *acids*. It melts at 162°, and solidifies to an amorphous mass on cooling; may be heated to 200° without decomposition; yields a slight sublimate when heated in a tube. It is coloured dark carmine-red by *sulphuric acid and manganic peroxide*. Its aqueous or alcoholic solution gives a dark cherry-red colour with *ferric chloride*. When heated with *hydrochloric* or *dilute sulphuric acid*, it is resolved into glucose and ononetin (p. 203).

**ONYX.** A chalcedonic variety of quartz, resembling agate, but having the colours—usually a light clear brown and an opaque white—arranged in flat horizontal planes. When the layers consist of sard and white chalcedony, the stone is called *sardonyx*.

**OOLITE** (from ὠόν an egg).—A lime-stone rock consisting of minute spherical grains resembling the roe of a fish. In some oolites the individual grains are formed of concentric layers enclosing a nucleus of some foreign substance; in the oolite of the Karlsbad springs, for example, this nucleus usually consists of granite.

**OOSITE.** A mineral resembling pinite from the porphyry of Oos near Geroldsan in Baden. Nessler (Jahresb. 1861, p. 1008) found in oosite from Gunzenbach and Selighofen, 58·69 silica, 2·289 alumina, 4·09 ferrous (= 4·54 ferric) oxide, 0·22 magnesia, 4·94 potash, 1·14 soda and 5·11 water (= 100·27).

**OPAL.** Native amorphous hydrated silica, occurring in masses having a conchoïdal fracture, vitreous lustre sometimes inclining to resinous or pearly, and white, yellow, brown, green, or grey colour according to the foreign substances present, sometimes exhibiting a rich play of colours, or different colours by refracted and reflected light. Hardness = 5·5—6·5. Specific gravity = 1·9—2·3. It appears to be a mixture of several hydrates of silica and various adventitious substances, such as ferric oxide, alumina, magnesia, alkalis, &c.; the proportion of silica varying from 73 to 95 per cent., and that of water from 3 to 12 per cent. Pulverised opal, like artificially prepared amorphous silica, dissolves in hot potash-ley, a character by which it is distinguished from quartz (crystallised silica). Opal is infusible before the blowpipe, but gives off water and becomes opaque. Some varieties containing iron turn red.

The following varieties of opal are distinguished according to their colour and other physical properties.—1. *Precious* or *noble opal:* generally white or colourless, and exhibiting a rich play of colours, green, red, blue, and yellow of various shades. When large and exhibiting its iridescence in perfection, it is a very valuable gem. It occurs in porphyry at Czernewitza near Kashan in Hungary, at Frankfort, and at Gracias à Dios in Hondnras.—2. *Fire opal* or *Girasol:* a transparent opal coloured hyacinth-red to honey- and wine-yellow by ferric oxide, sometimes with blue and yellow shades; occurs at Zimapan in Mexico and in the Faroe islands.—3. *Common opal:* of various colours, but only translucent or semi-transparent and without iridescence; abundant in Hungary, the Faroe islands, Iceland, the Giant's Causeway, and the Hebrides: found also near Smyrna.—4. *Hyalite:* mostly quite transparent and colourless, or enamel-like, but neither bright-coloured nor iridescent; occurs in amygdaloïd at Schemnitz in Hungary, and in clinkstone at Waltzsch in Bohemia; also in several localities in the United States.—5. *Semi-opal:* generally translucent at the edges only, and with a waxy, not glassy lustre; found near Hanau.—6. *Wood-opal* is a semi-opal having a peculiar ligneous structure, produced in fact by the silicatisation of fossil wood; it forms large trees in the pumice conglomerates of Saiba near Nensohl and Kremnitz in Hungary, in Faroe, near Hobart Town in Tasmania, and other trap-countries. The following varieties occur as concretions or coatings.—7. *Menilite:* brown opaque compact reniform masses, imbedded in adhesive slate at Menil Montant near Paris.—8. *Cacholong:* nearly opaque, of porcelain or bluish-white colour; adheres to the tongue, contains a small quantity of alumina with 3·5 per cent. water; it is closely allied to hydrophane, and often associated with it; occurs in loose masses in the river Cach in Bucharia.—9. *Opal-jasper* is a variety containing several per cent. of iron.—10. *Silicious sinter* is a loose silicious aggregate deposited by the Geysers of Iceland, where it presents porous, stalactitic, fibrous, cauliflower-like, and occasionally compact concretions, called *geyserite* by Damour.—11. *Pearl-sinter* or *Fiorite* occurs in the cavities of volcanic tufa, in smooth, shining, globular and botryoïdal masses, having a pearly lustre.—12. *Michaelite*, from the island of St. Michael in the Azores, is a white pearly variety; specific gravity 1·88.—13. *Alumocalcite* is an impure opal of a bluish milk-white colour containing 6 per cent. lime.—14. Some, if not all the silicious deposits formed of infusorial remains also consist of amorphous soluble silica (some, however, likewise contain quartz). *Randanite* (*silice gélatineuse*), occurring as a fine earth or in compact earthy masses at Cessat near Pont Gibaud (Dep. Puy-de-Dome) and in the neighbourhood of Algiers, is a variety of this kind.

Some varieties of opal are found, with galena and blende, in metalliferous veins; it also occupies the interior of fossils in sandstone. Its formation is due to the solubility of amorphous silica in water, especially in hot water or water containing carbonic acid, the silica being dissolved out by spring waters from decomposed silicates, and deposited under favourable circumstances in a state more or less approaching to purity.

**OPAL ALLOPHANE.** Syn. with SCHRÖTTERITE (*q. v.*);—also with chrysocolla or silicate of copper (see SILICATES).

**OPHIOLITE.** A name applied by T. S. Hunt (Sill. Am. J. [2] xxv. 217; Jahresb. 1859, p. 785) to serpentine (pure ophiolite) and its varieties (see SERPENTINE.

**OPHITE.** Syn. with SERPENTINE.

**OPHITONE.** This name is applied by Corenwinder (Jahresb. 1847–8, p. 1279) to the porphyry of Ternuay, a rock consisting essentially of felspar and augite.

**OPIAMMONE.** See OPIANIC ACID, AMIDES OF (p. 206).

**OPIANIC ACID.** $C^{10}H^{10}O^5 = \left.\begin{matrix}C^{10}H^9O^4\\ H\end{matrix}\right\}O$, or $\left.\begin{matrix}(C^8H^2O^2)^{iv}\\ (CH^3)^2H\end{matrix}\right\}\begin{matrix}H\\ O^3\end{matrix}$ (Liebig and Wöhler, Ann. Ch. Pharm. xliv. 126.—Wöhler, *ibid.* l. 1.—Blyth, *ibid.* l. 29.—Anderson, Edinb. Phil. Trans. xx. [2] 347.—Matthiessen and Foster, Chem. Soc. J. xvi. 345.)—An acid produced, together with cotarnine, by the oxidation of narcotine:

$$\underset{\text{Narcotine.}}{C^{22}H^{23}NO^7} + O = \underset{\text{Cotarnine.}}{C^{12}H^{13}NO^3} + \underset{\text{Opianic acid.}}{C^{10}H^{10}O^5};$$

*e. g.* by the action of sulphuric acid and peroxide of maganese or peroxide of lead; by the action of boiling nitric acid; by boiling hydrochlorate of narcotine with platinic chloride and water.—Also, by boiling teropiammone (triopianamide) with potash-ley.

The following is the mode of preparation recommended by Matthiessen and Foster: 100 grms. of narcotine is dissolved in a considerable excess of dilute sulphuric acid (150 grms. acid and 1500 grms. water); the solution is heated to boiling, and 150 grms. of finely powdered black oxide of manganese (containing 60 per cent. real peroxide) is added as quickly as possible, care being taken that it does not cause the liquid to froth over: when the whole quantity of peroxide has been added, the mixture is quickly filtered through a funnel surrounded with boiling water. The filtrate on cooling becomes half solid, from separation of crystals of opianic acid; and by twice recrystallising this product from boiling water it is obtained nearly pure, though still retaining a slight brownish colour, from which it may be freed, if necessary, by boiling with dilute hypochlorite of sodium, and decomposing the resulting solution with hydrochloric acid. The opianic acid is then deposited as the liquid cools, and may be recrystallised from boiling water.

*Properties.*—Opianic acid crystallises in thin prisms, often radiating and interlaced. It is colourless, has a bitter taste and slight acid reaction, dissolves sparingly in cold, easily in boiling water, also in alcohol and in ether. It melts at 140° without loss of weight, and is not volatile; but if more strongly heated in a retort, it creeps up the sides and may thus be distilled without actually volatilising. When heated in contact with the air, it gives off aromatic vapours which smell like vanilla, and burn with a smoky flame.

Opianic acid suffers a remarkable change under the influence of heat. The melted acid remains soft and transparent for some time after cooling, but ultimately loses its transparency, and becomes hard and milk-white. In this state it has the same composition as the crystallised acid, but differs from it considerably in its properties, being insoluble in water and alcohol, and even in dilute alkalis, dissolving only after prolonged boiling with caustic potash.

*Decompositions.*—1. Opianic acid heated with *nitric acid*, *platinic chloride*, or *sulphuric acid and peroxide of lead*, is converted into hemipinic acid, $C^{10}H^{10}O^6$.—2. When it is mixed with a large excess of potash-ley, and evaporated nearly to dryness, it is resolved into hemipinic acid and meconin: $2C^{10}H^{10}O^5 = C^{10}H^{10}O^6 + C^{10}H^{10}O^4$ (Matthiessen and Foster).—3. By the action of *nascent hydrogen*, as when its aqueous solution is warmed with *sodium-amalgam*, it is converted into meconin (Matthiessen and Foster):

$$C^{10}H^{10}O^5 + H^2 = C^{10}H^{10}O^4 + H^2O.$$

4. When fused in a current of dry *chlorine*, it gives off hydrochloric acid, and yields yellowish-red resinous products (Wöhler).—5. When heated with three or four times its weight of strong *hydrochloric acid*, either to 100° in a sealed tube, or to the boiling point of the acid in an open vessel, it is decomposed, with evolution of methylic chloride and carbonic anhydride, and formation of an acid containing $C^9H^8O^5$ (Mattthiessen and Foster):

$$C^{10}H^{10}O^5 + HCl = C^9H^8O^5 + CH^3Cl.$$

6. A similar decomposition appears to take place when opianic acid is boiled with fuming *hydriodic acid*, methylic iodide being given off without separation of iodine (Matthiessen and Foster).—7. *Sulphurous acid* dissolves opianic acid, producing opiano-sulphurous acid.—8. The aqueous solution of opianic acid does not appear to be altered by *sulphydric acid* at the boiling heat, but on cooling to 70° it is con-

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verted into **sulphopianic acid**, $C^{10}H^{10}SO^4$, without formation of any other product (Wöhler).

$$C^{10}H^{10}O^5 + H^2S = C^{10}H^{10}SO^4 + H^2O.$$

OPIANATES. $C^{10}H^9MO^5$ or $C^{20}H^{16}M''O^{10}$, according to the atomicity of the metal. A boiling solution of the acid decomposes the carbonates of barium, calcium, lead and silver, forming crystallisable salts.

The *ammonium-salt* is obtained in large tabular crystals by spontaneous evaporation of a mixture of alcohol and a saturated solution of opianic acid in ammonia. The ammoniacal solution unmixed with alcohol yields by evaporation an amorphous transparent mass, which dissolves but partially in water, leaving a residue of opiammone (*vid. inf.*).

The *barium-salt*, $C^{20}H^{16}Bba''O^{10}.2H^2O$, forms radiate prisms which effloresce with loss of 6 per cent. water (= 2 at.). The *calcium-salt* is soluble and crystallisable. The *lead-salt*, $C^{20}H^{16}Ppb''O^{10}.2H^2O$, forms shining, transparent, mammellated, sparingly soluble crystals, which melt at 150°, and begin to decompose at 180°. From hot solutions it sometimes crystallises in tufts of small silky prisms which are anhydrous. It is soluble in alcohol. The *silver-salt*, $C^{10}H^9AgO^5.xH^2O$, crystallises in transparent shortened prisms, which appear yellow in mass. They give off their water at 100°, and melt with decomposition at 200°.

*Opianate of Ethyl. Opianic Ether.* $C^{10}H^9(C^2H^5)O^5$.—Formed by passing sulphurous acid gas into a hot alcoholic solution of opianic acid, and deposited from the concentrated liquid in tufts of small prisms or in spherules (Wöhler). Or it may be produced by heating opianic acid with alcoholic hydrochloric acid to 100° in a sealed tube, precipitated by pouring the contents of the tube into water, and obtained by crystallisation from alcohol in hemispherical masses of brilliantly white radiating needles (Matthiessen and Foster). It is inodorous, but has a slightly bitter taste; is insoluble in water, but dissolves easily in alcohol and ether; melts at 92° (Wöhler); at 88° (Matthiessen and Foster), and solidifies in a radiated mass on cooling. It may be sublimed between two watch-glasses. When heated some degrees above its melting point, it remains for a long time soft and amorphous; it bears a high temperature without decomposition. (Wöhler.)

By boiling with water, it is slowly converted into alcohol and opianic acid, more quickly by potash. It is not attacked by ammonia in the cold. (Wöhler.)

### *Acids derived from Opianic acid.*

OPIANO-SULPHUROUS ACID, $C^{10}H^8SO^6$? (Wöhler, *loc. cit.*)—This acid, obtained by evaporating a solution of opianic acid in hot aqueous sulphurous acid, is a transparent, crystalline mass, which dissolves the carbonates of barium and lead, forming crystallised salts.—The *barium-salt* forms shining colourless rhomboïdal tablets which give off water and begin to decompose at 140°.—The *lead-salt* crystallises in four-sided prisms with dihedral summits and having their lateral edges replaced by broad faces, so that the crystals appear hexagonal. They give off 6·5 per cent., that is, half of their water of crystallisation at 130°, the rest with slight decomposition at 170°. The crystallised salt gave by analysis 29·23 per cent. carbon, 3·00 hydrogen, 8·10 sulphur, and 26·67 lead-oxide, agreeing approximately with the formula $C^{10}H^7PbSO^6.3H^2O$ (*vid.* Gerhardt, *Traité*, iv. 87).

SULPHOPIANIC ACID, $C^{10}H^{10}O^4S^2$, produced by the action of sulphydric acid on opianic acid (p. 205), forms delicate yellow prisms which soften below 100°, and becomes completely fluid at the temperature of boiling water, forming a pale yellow oil which on cooling solidifies in a transparent amorphous mass. This acid gives by analysis 52·4—53·0 per cent. carbon, 4·2 hydrogen, and 14·3 sulphur, the formula requiring 53·1 C, 4·4 H, 14·1 S and 28·4 O. (Wöhler.)

The acid decomposes above 100°, and when calcined, takes fire and burns with a sulphurous flame.

The amorphous acid dissolves in alkalis, and the solution of its ammonium-salt forms with lead- and silver-salts, precipitates which are easily decomposed when heated in the liquid.—The behaviour of the crystallised acid with bases has not been examined.

**OPIANIC ACID, AMIDES OF.** Two of these bodies are known, viz.:

$$\left.\begin{array}{l}\text{Diopianylamide}\\ \text{or Opiammone}\end{array}\right\} C^{20}H^{19}NO^8 = \left.\begin{array}{c}(C^{10}H^9O^4)^2\\ H\end{array}\right\} N = 2C^{10}H^{10}O^5 + NH^3 - 2H^2O.$$

$$\left.\begin{array}{l}\text{Triopianylamide}\\ \text{or Teropiammone}\end{array}\right\} C^{30}H^{29}NO^{13} = (C^{10}H^9O^4)^3N.H^2O = 3C^{10}H^{10}O^5 + NH^3 - 2H^2O.$$

Both these compounds are resolved by alkalis into opianic acid and ammonia, but only the first appears to be producible by the dehydration of opianate of ammonium.

Opiammone, $C^{20}H^{19}NO^{8}$.—A solution of opianic acid in ammonia leaves, when evaporated at a very gentle heat, an amorphous transparent mass, which becomes milk-white when treated with water and dissolves but partially, leaving opiammone. The dried residue may be completely converted into this compound by heating it to a temperature a little above 100°, as long as ammonia is given off, and the product may be freed from the last traces of opianate of ammonium by boiling with water.

Opiammone is a pale yellow crystalline powder, insoluble in cold *water*, and but little attacked by boiling water; but when heated with water to 150° in a sealed tube it dissolves completely, as opianate of ammonium. When heated it creeps along the sides of the vessel without subliming, but if strongly heated in contact with air, it decomposes. It is not altered by heating with dilute acids. *Caustic potash* slowly converts it, with evolution of ammonia, into opianate of potassium, and the potassium-salt of another acid not yet analysed, which Wöhler designates by the name xanthopenic acid. On adding hydrochloric acid to the solution, xanthopenic acid is precipitated in yellow flakes and the remaining liquid deposits crystals of opianic acid. (Wöhler, *loc. cit.*)

Teropiammone, $C^{60}H^{29}NO^{18}$, is produced by the action of dilute nitric acid upon narcotine; no other mode of preparing it has yet been discovered. It crystallises in slender colourless needles, insoluble in *water*, sparingly soluble in cold *alcohol*, rather more in boiling alcohol, very sparingly in *ether*. It is decomposed by *nitric* but not by hydrochloric acid. Strong *sulphuric acid*, dissolves it in the cold with yellow colour, but on heating the solution, it assumes a fine crimson tint. It is not attacked by ammonia. Boiling *potash* eliminates ammonia and converts it into opianate of potassium. (Anderson.)

**OPIANIC ETHER.** See p. 206.

**OPIANINE?** A base resembling narcotine, found by Hinterberger (Ann. Ch. Pharm. lxxvii. 207; lxxxii. 319) in some specimens of Egyptian opium. It was precipitated by ammonia from the aqueous extract together with morphine, and on dissolving this precipitate in alcohol, the opianine crystallised out first in large right rhombic prisms, which yielded by analysis 63·0 per cent. carbon, 5·7 hydrogen, and 4·3 (mean) nitrogen, whence Hinterberger deduces the formula $C^{66}H^{36}N^{2}O^{21}$ requiring 63·1 carbon, 5·8 hydrogen and 4·5 nitrogen. In one analysis however (by combustion with soda-lime), Hinterberger found only 2·2 per cent. nitrogen, and accordingly gave at first the formula $C^{66}H^{36}NO^{22}$; Anderson (Ann. Ch. Pharm. xcviii. 50) deduces from the same data the formula $C^{66}H^{37}NO^{22}$. Gerhardt (*Traité*, iv. 68) and Weltzien (*Organ. Verbind.* p. 567) doubt the existence of opianine as distinct from narcotine. Opianine forms, according to Hinterberger, a *chloromercurate* containing $C^{66}H^{36}N^{2}O^{21}.HCl.HgCl$. (See *Gmelin's Handbook*, xvi. 66.)

**OPIANO-SULPHUROUS ACID.** See p. 206.

**OPIANYL.** $C^{10}H^{9}O^{4}$.—A radicle which may be supposed to exist in opianic acid and its derivatives. Anderson applies the name to meconin, $C^{10}H^{10}O^{4}$.

**OPIUM.** This valuable drug is the dried juice obtained from the unripe capsules of the white poppy (*Papaver somniferum*), a plant extensively cultivated for the purpose in Asia Minor, Egypt, and Hindostan. Persia and Algeria likewise produce opium, and the plant has been cultivated, but not with very satisfactory results, in various parts of Europe. The European markets are supplied chiefly from Asia Minor and Egypt, the opium from the former locality, called Turkish or Smyrna opium, being the best, that is to say the richest in morphine. East Indian opium is chiefly exported to China. The opium is extracted by making incisions in the capsules just after the petals have fallen off. A milky juice then exudes which soon concretes; it is left to dry over night, then removed with a blunt knife and kneaded with water into cakes, which are then further dried. As thus prepared, it is brown and somewhat hard, has a bitter, acrid, nauseous taste, and a peculiar sickly odour. It softens with the heat of the hand; when more strongly heated it takes fire, but does not burn readily. For further particulars respecting the preparation and properties of opium, see Pereira's *Materia Medica;* also a paper by Dr. Eatwell in the Pharmaceutica Journal for 1852.]

Opium is a very complex substance containing several alkaloïds, two or three organic acids, and several neutral organic substances besides inorganic salts. The following is a list of its peculiar constituents:

| *Alkaloïds.* | | *Acids and Neutral Substances.* | |
|---|---|---|---|
| *Name.* | *Discovered by* | *Name.* | *Discovered by* |
| Narcotine | Derosne in 1804 | Meconic acid | Sertürner in 1804 |
| Morphine | Sertürner „ 1804 | Oily acid (Opium-fat) | Pelletier „ 1833 |
| Codeine | Robiqnet „ 1833 | Opium-resin | Pelletier „ 1833 |
| Narceine | Pelletier „ 1833 | Meconin | Duhlane „ 1833 |
| Pseudomorphine? | Pelletier „ 1835 | Porphyroxin? | Merck „ 1837 |
| Thebaine | Pelletier and Couerbe „ 1835 | Thebolactic acid? | T. & H. Smith „ 1862 |
| Papaverine | Merck „ 1840 | | |
| Opianine? | Hinterberger „ 1851 | | |

All the alkaloïds in the preceding list, except *papaverine* and *thebaine*, have been already described; the existence of pseudomorphine and opianine is very doubtful (see iii. 1051 and iv. 208). The following table exhibits a general view of the reactions of the opium-alkaloïds with various solvents:

*Solubility of Opium-alkaloïds.*

| Name. | Formula. | Reaction with | | | |
|---|---|---|---|---|---|
| | | *Water.* | *Alcohol.* | *Ether.* | *Potash.* |
| Morphine. | $C^{17}H^{19}NO^{3}$. | Very sparingly soluble. | Moderately soluble. | Nearly insoluble. | Soluble in excess. |
| Codeine. | $C^{18}H^{21}NO^{3}$. | Soluble. | Very soluble. | Very insoluble. | Insoluble in strong potash. |
| Thebaine. | $C^{19}H^{31}NO^{3}$. | Insoluble. | Soluble. | Soluble. | Soluble in dilute potash. |
| Papaverine. | $C^{20}H^{21}NO^{4}$. | Insoluble. | Soluble. | Soluble. | Insoluble. |
| Narceine. | $C^{23}H^{29}NO^{9}$. | Very sparingly soluble. | Soluble. | Insoluble. | Soluble in dilute potash. |
| Narcotine. | $C^{22}H^{23}NO^{7}$. | Nearly insoluble. | Soluble. | Soluble. | Insoluble. |

*Meconic acid* and *meconin* have been already described (iii. 859, 861). Pelletier's *opium-fat* and *opium-resin* will be described further on.

*Porphyroxin* is the name given by Merck (Ann. Ch. Pharm. xxi. 201) to a neutral crystalline substance which he obtained, to the amount of ½ per cent., from East Indian and Smyrna opium; but its existence is not well established. Anderson, who sought for it with some care, was unable to obtain it.

*Thebolactic acid* is an acid isomeric with lactic acid, said to exist in Turkey opium to the amount of 2 per cent., and to be separated from the impure mother-liquors of morphine by the ready crystallisability of its calcium-salts. Stenhouse regards it as identical with lactic acid, but some of its salts, especially the copper and morphine-salts, are said by its discoverers to differ in character from the corresponding lactates. The ferric salts of the two acids are likewise said to differ in their reaction with ammonia. Anderson was not able to detect the existence of thebolactic acid in opium.

Opium likewise contains gum, caoutchouc or a similar substance, vegetable albumin, cellulose, and a volatile odoriferous principle. Its inorganic constituents are potash, soda, ammonia, lime, magnesia, alumina (?) and ferric oxide, combined with hydrochloric, sulphuric, phosphoric, and silicic acids.

The proportions of these several constituents vary greatly in opium from different localities. The quantity of morphine, on which the commercial value chiefly depends, varies from 3 or 4 to 14 or 15 per cent. Smyrna opium generally contains, in the dry state, from 12 to 14 per cent. morphine (Guibourt); Egyptian, in the dry state, from 5·8 to 6·6 per cent. (Guibourt). Merck, however, found 6 to 7 per cent. in the undried substance; East Indian opium contains from 5·3 to 7·7 per cent. (Guibourt); in a dried sample of Persian opium Guibourt found 11·37 per cent. morphine and 8·17 narcotine. Algerian opium containing 7·6 per cent. water was found by Aubergier (Ann. Ch. Phys. [3] xx. 303) to contain the following proportions of morphine: opium from white poppies, 1·52 to 8·57 per cent.; from red poppies, 10·37 to 11·23 per cent.; from purple poppies, 14·71 to 17·83 per cent. In dry opium gathered at Erfurt from the blue poppy, Biltz found 16·6 and 20 per cent.; in that from the white poppy, 6·85 per cent. morphine. French varieties when dried contain on the average 17·7 per cent. morphine (maximum 22·9; minimum 14·8) (Guibourt). Opium collected at Brest in 1852 contained 8·2 per cent. (Roux, Compt. rend. xl. 34); that from Amiens in 1853 contained 14·75; and that from the same place in 1854, contained 16 per cent. morphine. (Descharmes and Benard, Compt. rend. xl. 34.—*Gmelin's Handbook*, xvi. 415.)

The following method of extracting the alkaloïds of opium and determining their relative quantities is given by Anderson (Chem. Soc. J. xv. 448). The morphine, codeine and meconic acid are first separated by the Robertson-Gregory process which consists in treating the aqueous extract of opium with chloride of calcium, whereby the meconic acid is precipitated as a calcium-salt, while the bases remain in solution as hydrochlorates, among which the morphine and codeine salts are easily crystallisable and separate from the concentrated solution, leaving the other bases in the mother-liquor. The morphine and codeine are then separated by ammonia as already described (iii. 1051).

To obtain the other bases, the black treacly mother-liquor is diluted with water and mixed with ammonia, which throws down a copious dark brown precipitate consisting of narcotine, papaverine and thebaine, accompanied by a small quantity of codeine, and contaminated with a brown resinous substance. This precipitate, which is at first quite granular, runs together, if allowed to remain in the liquid, into a resinous mass, whereby the mother-liquor is squeezed out of it as effectually as if it were put into a powerful press. The solution of this precipitate in boiling spirit deposits, on cooling, impure crystals of narcotine, which may be purified by successive crystallisations, with aid of animal charcoal. A further crop of crystals is obtained by distilling down the solution, and finally there remains a black mother-liquor, from which thebaine and papaverine may be prepared. For this purpose water is added; the liquid is slightly acidulated with acetic acid; the resin thereby separated is filtered off; basic acetate of lead is then added to the filtrate till it exhibits an alkaline reaction; and, the precipitate being separated, the excess of lead is removed by sulphydric, or more conveniently by sulphuric acid; ammonia then precipitates the thebaine, still mixed with resinous matters, from which it may be separated by crystallisation from alcohol; it can then be decolorised by animal charcoal. Papaverine may be extracted from the lead-precipitate by digesting it in alcohol, evaporating the liquid, treating it with hydrochloric acid, filtering from resin, concentrating, and leaving the solution to itself for some time, when the sparingly soluble hydrochlorate of papaverine slowly crystallises. From this salt the base may be obtained in a state of purity by precipitation with ammonia and crystallisation from spirit.

The mother-liquor from which the precipitate of these bases has been separated contains narceine and meconin, with a small quantity of papaverine. On concentrating it, narceine separates in abundance, and is easily obtained pure by washing with a small quantity of cold water, and crystallising two or three times. After concentrating the liquid till the narceine is completely separated, the residue is repeatedly agitated with $\frac{1}{3}$ of its volume of ether at 26°, which extracts meconin, together with a little papaverine; and the ether is distilled off from the extracts, a brown syrup then remaining. On treating this syrup with hydrochloric acid, papaverine dissolves, and meconin remains in the form of a dark grey crystalline powder, which may be freed from resin by repeated crystallisation from boiling water with addition of animal charcoal.

For Pelletier's method of separating the several constituents of opium, see *Gmelin's Handbook*, xvi. 420. For the estimation of morphine in opium, *ibid.* p. 423, or this Dictionary, iii. 1053.

On the microscopic appearances of the several constituents and medicinal preparations of opium, see Deane and Brady (*On Microscopical Research in relation to Pharmacy*, Chem. Soc. J. xviii. 34); also Helvig (*Das Mikroscop in der Toxicologie*, Maintz, 1864).

The following table exhibits the composition of five sorts of Smyrna opium as determined by Mulder (Handw. d. Chem. v. 721).

*Analyses of Smyrna Opium.*

| | | | | | |
|---|---|---|---|---|---|
| Morphine | 10·8 | 4·1 | 9·9 | 2·8 | 3·8 |
| Codeine | 0·7 | 0·8 | 0·8 | 0·9 | 0·6 |
| Narcotine | 6·8 | 8·2 | 9·6 | 7·7 | 6·5 |
| Narceine | 6·7 | 7·5 | 7·7 | 9·9 | 13·2 |
| Meconin | 0·8 | 0·8 | 0·3 | 1·4 | 0·6 |
| Meconic acid | 5·1 | 4·0 | 7·6 | 7·3 | 6·6 |
| Fat | 2·2 | 1·4 | 1·8 | 4·2 | 1·5 |
| Caoutchouc | 6·0 | 5·0 | 3·7 | 3·8 | 3·2 |
| Resin | 3·6 | 2·0 | 4·1 | 2·2 | 1·8 |
| Gummy extract | 25·2 | 31·5 | 21·8 | 22·6 | 25·7 |
| Gum | 1·0 | 2·9 | 0·7 | 3·0 | 0·9 |
| Vegetable mucus | 19·1 | 17·1 | 21·1 | 18·5 | 18·0 |
| Water | 9·8 | 12·2 | 11·4 | 13·0 | 14·0 |
| Loss | 2·2 | 2·5 | . . | 2·7 | 3·6 |
| | 100 | 100 | 100·5 | 100 | 100 |

In these analyses the proportion of narceine appears to be too high; possibly the thebaine and papaverine, the amounts of which are not specified, were weighed with it.

The following analyses are by Schindler (*loc. cit.*):

| | Opium from Smyrna. | Opium from Constantinople. | Opium from Egypt. |
|---|---|---|---|
| Morphine | 10·30 | 4·50 | 7·00 |
| Codeine | 0·25 | 0·52 | |
| Narcotine | 1·30 | 3·47 | 2·68 |
| Narceine | 0·71 | 0·42 | |
| Meconin | 0·08 | 0·30 | |
| Meconic acid | 4·70 | 4·38 | |
| Peculiar resin | 10·93 | 8·10 | |
| Vegetable mucus, caoutchouc, acid fat, and vegetable fibre | 26·25 | 17·18 | |
| Brown acid soluble in water and in alcohol | 1·04 | 0·40 | |
| Brown acid soluble only in water, and gum | 40·13 | 56·46 | |
| Lime | 0·40 | 0·02 | |
| Magnesia | 0·07 | 0·40 | |
| Alumina, ferric oxide, silica, calcic phosphate | 0·24 | 0·22 | |
| Salts, and volatile oil (about) | 0·36 | 0·36 | |
| | 96·76 | 96·73 | |

**OPIUM FAT.** *Oily acid of Opium.* $C^6H^{12}O$?—This substance, discovered by Pelletier, is obtained by repeatedly digesting opium-marc in warm alcohol of specific gravity 0·84, filtering each time after cooling, to separate the deposited caoutchouc, and distilling the alcohol down to three-fourths, filtering again to remove the narcotine which crystallises out, evaporating the filtrate to dryness, again exhausting the residue with hot alcohol of specific gravity 0·84, and repeating these operations till all the narcotine is removed. The residue left on evaporating the filtered solution is then exhausted with boiling water, and afterwards with ether, which takes up the oily acid, leaving opium-resin undissolved. The ethereal solution when evaporated leaves the oily acid in the liquid form, but still slightly contaminated with narcotine, which may be removed by agitation with water containing a little hydrochloric acid; the fat then floats on the surface and may be skimmed off.

Opium-fat is generally yellowish or brownish, the colour being probably due to impurities. It is soft, almost liquid, has a sharp burning taste, and an acid reaction not removed by repeated washing. It dissolves in alcohol, ether, and oils, and forms soaps with alkalis. (Pelletier, Ann. Ch. Pharm. l. 276.)

**OPIUM-MARC.** The residue of opium left after removal of the meconates of morphine and codeine and other salts soluble in water.

**OPIUM-RESIN.** $C^8H^{13}NO^3$?—This substance, the preparation of which has been described in connection with opium-fat, is brown, destitute of taste and odour, and becomes nearly fluid when warmed. At a higher temperature it swells up strongly, giving off large quantities of empyreumatic oil and combustible gases. It is insoluble in water, soluble in alcohol and in alkalis. (Pelletier, *loc. cit.*)

**OPOBALSAM.** Syn. with Mecca Balsam (see BALSAMS, i. 495).

**OPODELDOC.** *Linimentum saponato-camphoratum.*—A solution of soap in alcohol, with the addition of camphor and volatile oils. It is used externally against rheumatic pains, sprains, bruises, and other like complaints.

**OPOPANAX.** A concrete gummy resinous juice, obtained from the roots of an umbelliferous plant, the *Pastinaca Opopanax*, L., *Opopanax Chironium*, Koch, which grows spontaneously in the warmer countries, and bears the colds of our climate. The juice is brought from Turkey and the East Indies, sometimes in round drops or tears, but more commonly in irregular lumps, of a reddish-yellow colour on the outside, with specks of white; inwardly of a paler colour, and frequently variegated with large white pieces. It has a peculiar strong smell, and a bitter, acrid, somewhat nauseous taste. Its constituents are, resin 42·0 per cent., gum 33·4, ligneous matter 9·8, starch 4·2, malic acid 2·8, extractive matter 1·6, wax 0·3, caoutchouc a trace, volatile oil or loss 3·9. (Pelletier.)

The resin of opopanax melts at 100°, decomposes at a somewhat higher temperature, and contains, according to Johnston, 63·2—64·0 per cent. carbon and 6·7 hydrogen, agreeing approximately with the formula $C^{20}H^{24}O^7$ (63·8 C, 6·4 H, and 29·8 O).

**OPSIMOSE.** Beudant's name for partially altered Fowlerite from Franklin, New Jersey.

**ORANGE.** See CITRUS (i. 1002).

**ORANGITE.** See THORITE.

**ORCEIN.** $C^7H^7NO^3$. *Lichen-red. Flechtenroth.* (Robiquet, Ann. Ch. Phys. [2] xlii. 245; lviii. 320.—Heeren, Schw. J. lix. 336.—Dumas, Ann. Ch. Pharm. xxvii. 145.—Kane, Phil. Trans. 1840, p. 285.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 315.)—A compound formed from orcin by the action of ammonia and oxygen. It is prepared as follows: a small dish containing powdered orcin is placed above a vessel containing strong ammonia, and the whole is covered with a bell-jar. In the course of 24 hours the transformation is complete. The product may then be dissolved in water, and poured into a solution of hydrochloric acid which precipitates the orcein in red flocks, of a fine red colour. Orcein is present, together with other colouring matters, in the archil of commerce.

Orcein is uncrystallisable. It dissolves sparingly in *water*, imparting however its colour, and is precipitated from the solution by neutral salts. It is very soluble in *alcohol*, forming a deep scarlet solution from which it is precipitated by water. It dissolves in aqueous fixed *alkalis* with violet-red colour: the *ammoniacal* solution is of a very rich pansy colour. Orcein is separated by acids from its combinations with alkalis. *Sulphide of ammonium* destroys the colour of the ammoniacal solution, producing a brownish-black liquid, which, however, recovers its red colour on exposure to the air.

When a piece of *zinc* is plunged into an ammoniacal solution of orcein to which a slight excess of hydrochloric acid has been added, the liquid is completely decolorised, and when mixed with a certain quantity of ammonia deposits a white powder, leucorcein, which by contact with the air soon assumes a deep purple tint.

Orcein mixed with water or dissolved in ammonia is converted by contact with *chlorine*, into chlororcein, which is soluble in alcohol, ether, and in ammoniacal water, colouring the last-mentioned liquid brown.

**ORCHELLA WEEDS.** The cylindrical and flat species of *Roccella* used in the manufacture of orchil and cudbear are so called by the makers (see *Ure's Dict. of Arts, &c.*, iii. 311).

**ORCHIL.** Syn. with ARCHIL (i. 355).—An improved method of preparing this dye, introduced by Dr. Stenhouse, consists in treating the colour-yielding lichens, on the spot, with an alkali (potash or lime) to extract the colouring acids, and precipitating these acids with hydrochloric or acetic acid; they are thus completely separated from the woody fibre and other impurities.

Respecting the improved orchil-dye called "French Purple," see DYEING (ii. 356), also Hofmann's *Report on Chemical Products, &c., in the International Exhibition of* 1862, p. 117.

**ORCHIS.** The root of *Orchis fusca* contains coumarin, 2·47 grammes of which may be obtained from a kilogramme of it. (G. and C. Bley, Jahresb. 1857, p. 484.)

**ORCIN.** $C^7H^8O^2$. (Robiquet, Ann. Ch. Phys. [2] xlii. 245; lviii. 320.—Liebig and Will, Ann. Ch. Pharm. xxvii. 147.—Dumas, *ibid.* xxvii. 140.—Schunck, *ibid.* xli. 159; liv. 269.—Gerhardt, Compt. chim. 1845, p. 287.—Stenhouse, Phil. Trans. 1848, p. 85; Ann. Ch. Pharm. lxviii. 93, 99; Proc. Roy. Soc. xii. 263; Chem. Soc. J. xvi. 327.—De Luynes, Ann. Ch. Pharm. cxxviii. 330; cxxx. 31.—Lamparter, *ibid.* cxxxiv. 256.—Gm. xii. 353.—Gerh. iii. 810.)—This substance, discovered in 1829 by Robiquet in *Variolaria dealbata*, appears to exist ready formed in all the lichens used for the preparation of archil and litmus. It is formed artificially: 1. By boiling orsellic acid with water, and therefore also by boiling lecanoric (α-orsellic) acid, erythric acid (erythrin), picroerythrin, or evernic acid, with aqueous alkalis, these latter substances (except picroerythrin), being first converted into orsellic acid. Its formation from orsellic acid is represented by the equation,

$$\underset{\text{Orsellic acid.}}{C^8H^8O^4} = \underset{\text{Orcin.}}{C^7H^8O^2} + CO^2;$$

from picroerythrin by the equation,

$$\underset{\text{Picroerythrin.}}{C^{12}H^{16}O^7} + H^2O = \underset{\text{Erythro-mannite.}}{C^4H^{10}O^4} + \underset{\text{Orcin.}}{C^7H^8O^2} + CO^2.$$

2. By the dry distillation of lecanoric acid, erythric acid, evernic acid or picroerythrin.

3. Together with paraoxybenzoic acid, by melting aloes with hydrate of potassium probably thus:

$$\underset{\text{Aloeretic acid.}}{C^{15}H^{16}O^7} + O = \underset{\text{Orcin.}}{C^7H^8O^2} + \underset{\text{Paraoxy-benzoic acid.}}{C^7H^6O^3} + CO^2 + H^2O.$$

A pound of aloes thus treated yields from 9 to 11 grammes of orcin. (**Hlasiwetz** and **Barth**, Ann. Ch. Pharm. cxxxiv. 287.)

*Preparation.*—1. Dry *Variolaria dealbata* is exhausted with boiling alcohol; the solution freed by evaporation and cooling from the resin which separates; the remaining liquid evaporated to an extract; and this extract exhausted with water. The aqueous solution evaporated to a syrup, deposits after a few days crystals of orcin, which may be purified by recrystallisation from water, with addition of animal charcoal, during which operation, however, the charcoal absorbs a considerable quantity of orcin. (**Robiquet.**)

2. A *roccella* or a *lecanora* is macerated with milk of lime; the strained liquid boiled for a few hours in an open vessel, and evaporated to one-fourth; carbonic acid gas passed through it as long as a precipitate of calcic carbonate continues to form; and the filtrate evaporated to dryness over the water-bath. The residue is boiled with three or four times its bulk of strong alcohol; the solution evaporated, filtered and set aside to crystallise; the dark-coloured crystals are dried after three or four days between paper and dissolved in three or four times their volume of anhydrous ether; and the filtered solution is left to evaporate in vacuo. The large six-sided crystals thus obtained become still paler by crystallisation (**Stenhouse**). This method is well adapted for preparation on the large scale. **De Luynes** recommends heating erythric acid (the extract of *Roccella tinctoria*, &c.) with lime to 150° under pressure.

Perfectly colourless orcin may be obtained by the following methods: 3. Orsellic or erythric acid is boiled with water for half an hour or an hour, whereupon a large quantity of carbonic anhydride is given off, and the evaporated solution (mixed perhaps with animal charcoal) deposits on cooling a large quantity of colourless crystals of orcin (**Stenhouse**).—4. Lecanoric acid (or its green mother-liquor) is boiled with strong baryta-water; the baryta precipitated by carbonic acid; and the liquid heated to the boiling point, then filtered and left to evaporate. The crystals thus obtained are usually coloured, but may be purified by boiling with aluminic or ferric hydrate, which takes up the colouring matter. If the orcin still remains coloured it must be distilled from a retort, the distillation being interrupted as soon as the orcin vapours begin to carry colouring matter over with them. The aqueous solution of the distillate yields colourless crystals by evaporation (**Schunck**). See also **Lamparter** (Ann. Ch. Pharm. cxxxiv. 256).

*Properties.*—Orcin crystallises from its aqueous solution evaporated to a syrup in colourless six-sided monoclinic prisms, exhibiting the combination $\infty P \,.\, \infty P\infty \,.\, - P\infty$, sometimes with $oP$. Angle $\infty P : \infty P$, in the orthodiagonal principal section $= 102° 24'$; $\infty P\infty : oP = 83° 57'$; $\infty P\infty : - P\infty = 136° 16'$. Cleavage parallel to $\infty P\infty$. The crystals are very soluble in *water* and in *alcohol;* they dissolve also in *ether*. The aqueous solution is neutral to test-paper, and has a strongly saccharine, somewhat nauseous taste. The crystals deposited from it contain 12·67 per cent. (1 at.) water, which they give off entirely in vacuo over oil of vitriol, or at the temperature of the water-bath. From anhydrous ether, orcin is deposited in anhydrous crystals.

Hydrated orcin melts below 100°, giving off its water of crystallisation. Anhydrous orcin heated quickly to 290°, distils in the form of a syrupy liquid, which gradually absorbs moisture from the air and becomes crystalline. When gently heated in shallow vessels, it may be sublimed in needles. Its vapour-density, according to Dumas' determination, is 5·7, which agrees exactly with that required by calculation.

The aqueous solution of orcin is not precipitated by mercuric chloride, neutral acetate of lead, cupric sulphate, gelatin or tannin. With *basic acetate of lead*, however, it gives a white precipitate which appears to contain $C^7H^6Pb''O^2.Pb''O$; and is likewise produced on adding nitrate of lead to an ammoniacal solution of orcin. With *ferric chloride*, it forms a dark red or nearly black precipitate, from which ammonia extracts orcin. It does not precipitate *nitrate of silver* except on addition of ammonia.

Melted orcin decomposes dry *carbonate of sodium*, with evolution of carbonic anhydride. Aqueous orcin added to a solution of *silicate of sodium*, precipitates silica; and a crystal of orcin thrown into a boiling solution of sodic silicate is converted, without alteration of form, into gelatinous silica. A concentrated and slightly acid solution of *sulphate of quinine* or *cinchonine* becomes turbid when mixed with a concentrated aqueous solution of orcin, with separation of an oily compound of the base with orcin which becomes nearly solid on exposure to the air. (De Luynes.)

*Decompositions.*—1. Orcin gradually turns red in contact with *air*, especially in sunlight.—2. Orcin dissolves in *nitric acid*, and on heating the solution nitrous fumes are evolved, the liquid turning red, and depositing a red resinous substance soluble in alcohol and in acids. If the action of the acid be prolonged, the product is wholly converted into oxalic acid. Orcin takes fire when very strong nitric acid is poured upon it, but when it is gradually added to cooled fuming nitric acid, it dissolves without evolution of red vapours, and water precipitates from the solution a red mass soluble in alkalis. When the vapour of ordinary nitric acid (of 40° Bm.) is made to act slowly upon orcin, the crystals become first brown, then red, and are converted into a colouring matter different from orcein. This red product is soluble in water, alcohol and ether; dyes silk and wool red without the aid of a mordant; is coloured transiently red by ammonia, permanently by fixed alkalis, and is restored to its original light red colour by the action of acids. Its aqueous solution is precipitated by common-salt, but the colouring matter redissolves in water after the salt has been washed out.

3. Orcin heated with solution of *acid chromate of potassium*, yields a brown substance whose decomposition is accelerated by addition of sulphuric acid.—4. Solution of *chloride of lime* colours orcin deep violet, the tint gradually changing to brown, and ultimately to yellow.—5. The aqueous solution of orcin mixed with caustic *potash* or *soda*, quickly attracts oxygen and acquires a red or brown colour.—6. Dry *ammonia gas* is absorbed by orcin in large quantity, but is given off again on exposure to the air. When orcin is placed under a bell-jar, together with a basin containing *aqueous ammonia*, it gradually turns dark brown, and is converted into orcein (p. 211).

$$C^7H^8O^2 + NH^3 + O^3 = C^7H^7NO^3 + 2H^2O.$$

7. The precipitate which orcin forms with *ammonio-nitrate of silver* is reduced by boiling, with formation of a silver speculum, the liquid at the same time turning red.—8. *Tri-chloride of gold* is reduced by aqueous orcin, slowly in the cold, immediately when heated, a dark brown powder separating at the same time. (Schunck.)

9. Orcin heated to 60°—80° with strong *sulphuric acid* is partly converted into orcin-sulphuric acid, $C^7H^8S^2O^8$. On diluting the resulting black liquid with water, saturating with carbonate of lead, and quickly evaporating over the water-bath, a crystalline mass is obtained consisting chiefly of unaltered orcin; and when this is removed by digestion with ether, a residue is left, the hot aqueous solution of which saturated with carbonate of lead and filtered, deposits after a few hours, brownish, nacreous, rectangular laminæ, consisting of basic orcin-sulphate of lead, $C^7H^6Ppb''S^2O^8.Ppb''H^2O^2.\frac{1}{2}H^2O$. The mother-liquor of these crystals yields a second salt in microscopic prisms, containing $2C^7H^6Ppb''S^2O^8.Ppb''H^2O^2.6H^2O$. (Hesse, Jahresb. 1861, p. 701.)

### *Substitution-derivatives of Orcin.*

Orcin forms substitution-derivatives with *chlorine*, *bromine*, and *iodine*. The chlorinated and brominated compounds are obtained by the direct action of chlorine and bromine on orcin, the iodine-compound ($C^7H^5I^3O^2$) by the action of trichloride of iodine: iodine itself does not act upon orcin.

**Bromorcin.** $C^7H^7BrO^2$. (Lamparter, Ann. Ch. Pharm. cxxxiv. 258.)—Obtained by adding bromine-water to aqueous orcin, so long as little or no precipitate is thereby produced, or better, by mixing the two liquids in quantities containing 2 at. bromine to 1 at. orcin. The resulting solution yields by evaporation hard anhydrous rhombic crystals of bromorcin, which may be purified by recrystallisation from water.

Bromorcin is moderately soluble in hot, less soluble in cold *water*, extremely soluble in *alcohol* and *ether*. Caustic *potash* dissolves it with decomposition and brown coloration. It melts at 135°, begins to sublime below 100°, and decomposes at higher temperatures. When mixed with *basic acetate of lead*, it yields a white precipitate, from which it is separated in its original state by sulphydric acid.

**Tribromorcin.** $C^7H^5Br^3O^2$. *Bromorceïd.* (Stenhouse, Phil. Trans. 1848, p. 87.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 317.—Lamparter, Ann. Ch. Pharm. cxxxiv. 257.)—This compound is formed, together with a brown resin, when bromine in excess is added to orcin or its concentrated aqueous solution (Stenhouse; Laurent and Gerhardt); but by adding bromine-water to an aqueous solution of orcin, the same compound is obtained, uncontaminated with resin, as a nearly colourless crystalline precipitate, which may be further purified by recrystallisation from weak spirit (Lamparter). It is also produced by the action of bromine on orsellic acid. (Hesse, Ann. Ch. Pharm. cxvii. 297.)

Tribromorcin crystallises in fine colourless silky needles (Lamparter), in reddish-white prisms (Hesse). It melts at 103° (Lamparter); at 98° (Hesse). It is insoluble in *water*, very soluble in *alcohol* and *ether*. It decomposes at high temperatures, giving off hydrobromic acid, and yielding an oily distillate which solidifies on cooling, together with a copious residue of charcoal. *Potash* poured upon tribromorcin colours it deep violet-brown, and on diluting with water, the whole dissolves with brownish-red colour. *Ammonia* does not produce this coloration. *Acids* destroy the colour of the potassic solution.

Tribromorcin treated with *bromine* yields an easily fusible resinous mass having an extremely disagreeable pungent odour, and probably identical with the resinous body obtained by Stenhouse, and by Laurent and Gerhardt in the preparation of tribromorcin. 1 at. orcin treated with 4 at. bromine also yields a black resinous mass. (Lamparter.)

**Trichlororcin.** $C^7H^5Cl^3O^2$. *Chlororceïd* (Schunck, Ann. Ch. Pharm. liv. 271. —Stenhouse, Phil. Trans. 1848, p. 88.—De Luynes, Ann. Ch. Pharm. cxxx. 34).—Stenhouse and Schunck, by treating orcin with chlorine gas, obtained a crystalline chlorinated compound contaminated with a dark brown resin, somewhat difficult to separate; the crystalline product was not analysed. De Luynes, by treating orcin with hydrochloric acid and chlorate of potassium, obtains a product having the same physical properties, uncontaminated with resin, and exhibiting by analysis the composition of trichlororcin. It is soluble in boiling *water*, and in *alcohol*, from which it crystallises in colourless needles; melts at about 159°; volatilises partially without decomposition; dissolves in *alkalis;* does not precipitate an alcoholic solution of silver-nitrate.

**Tri-iodorcin.** $C^7H^5I^3O^2$ (Stenhouse, Chem. Soc. J. xvii. 327).—Produced by the action of trichloride of iodine on aqueous orcin. The trichloride is added to the dilute aqueous solution in quantity not quite sufficient to precipitate the whole of the orcin; the brownish-yellow adhesive mass which collects at the bottom is washed with water, dried, and dissolved in sulphide of carbon; and the solution is filtered to separate a dark brown resinous substance; the greater part of the sulphide of carbon is then removed by distillation, and the crystals obtained on the cooling of the solution are drained from the dark mother-liquor, washed with a small quantity of cold sulphide of carbon, pressed between bibulous paper, and twice recrystallised from boiling spirit.

Tri-iodorcin thus obtained crystallises in large transparent, brittle plates, tinged with brown, and somewhat resembling chloride of barium. They are very soluble in sulphide of carbon, still more so in ether, moderately soluble in alcohol, insoluble in water. Heated to 100° they gradually become brown. They dissolve in caustic *alkalis*, decomposing, however, and forming deep brown solutions. Strong *nitric acid* decomposes them, slowly in the cold, rapidly on heating, with evolution of nitrous fumes and iodine vapour. *Sulphuric acid* does not act upon them in the cold, but on the application of heat the crystals char and give off vapour of iodine.

### *Compounds homologous with Orcin.*

**Beta-orcin.** $C^8H^{10}O^2$? (Stenhouse, Phil. Mag. [3] xxxiii. 300; Ann. Ch. Pharm. lxviii. 104).—This compound is produced from usnic acid, by the action of heat or by boiling with caustic alkalis or alkaline earths. Usnic acid submitted to dry distillation yields a sublimate together with an empyreumatic liquid and a large carbonaceous residue. On treating the entire distillate with water and evaporating to a syrup, the residue deposits after some days brown crystals of β-orcin, which may be purified by treatment with animal charcoal, and repeated crystallisation from weak spirit. The treatment of usnic acid with alkalis is a less advantageous mode of preparation, as a considerable portion of the product is then converted into resin.

Beta-orcin forms shining crystals belonging to the dimetric system, and often of considerable size. Observed combination $\infty P . P . \frac{1}{2}P . oP . \infty P\infty . P\infty$. Angle $\frac{1}{2}P : oP = 130° 57'$; $P : oP = 113° 27'$; $P\infty : oP = 120° 31'$; $P : \infty P = 156° 33'$; $\frac{1}{2}P : \infty P = 139° 3'$; $P\infty : \infty P\infty = 148° 29'$. No perceptible cleavage (Miller). It is moderately soluble in cold *water*, but less so than orcin, easily soluble in boiling water, also in *alcohol* and in *ether*. It has a slightly saccharine taste, and is neutral to reagents. It sublimes unaltered, easily takes fire and burns with a smoky flame.

Dried in vacuo, it gave by analysis 68·84—69·20 per cent. carbon, and 7·22—7·50 hydrogen, whence Stenhouse deduced the formula $C^{19}H^{24}O^5$, requiring 68·68 C, 7·22 H, and 24·10 O. Gerhardt (*Traité*, iii. 321) proposed the formula $C^8H^{10}O^2$ (requiring

69·56 C, 7·24 H, and 23·20 O), according to which the compound is homologous with orcin, and metameric with anisic alcohol. Strecker (Ann. Ch. Pharm. lxviii. 114) had previously suggested the formula $2C^{17}H^{18}O^{3}.3H^{2}O$ (requiring 68·7 C, and 7·1 H), according to which, its formation from usnic acid (supposing the latter to be $C^{19}H^{18}O^{7}$) would be represented by the equation: $C^{19}H^{18}O^{7} = C^{17}H^{18}O^{3} + 2CO^{2}$.

The crystals of β-orcin do not lose anything in a vacuum over oil of vitriol; but when heated over the water-bath, they give off a considerable quantity of water. They do not melt at 109°.

Beta-orcin treated with *ammonia* acquires a splendid red colour in a few minutes, the effect taking place much more quickly than with orcin. With solution of *hydrate or carbonate of potassium*, it forms a substance of a fine purple colour. Solution of *chloride of lime* colours it blood-red, not violet like orcin.

The alcoholic solution of β-orcin does not precipitate silver-nitrate, either pure or mixed with ammonia, nor the salts of barium, lead, iron, or copper. It does not precipitate neutral acetate of lead, but with the *basic acetate*, it forms a copious precipitate which is soluble in excess of the lead-solution, and quickly acquires a deep red colour on exposure to the air.

2. **Resorcin.** $C^{6}H^{6}O^{2}$ (Hlasiwetz and Barth, Ann. Ch. Pharm. cxxx. 354).—A compound, isomeric with pyrocatechin and hydroquinone, produced by the action of melting potash on galbanum. To prepare it, the resin, freed by alcohol from its gummy constituents, is fused with 2½ to 3 pts. hydrate of potassium till the mass becomes homogeneous. Water is then added, the liquid acidulated with sulphuric acid, and filtered when cold; the filtrate shaken two or three times with ether; the etheral solution distilled; and the residue, after being evaporated to a certain extent over the water-bath, is introduced into a retort and distilled over an open fire. The first portion of the distillate is watery and contains volatile acids; but afterwards an oily liquid passes over which soon solidifies in radiating crystals. The product may be freed from adhering volatile acids by dissolving it in a small quantity of warm water, supersaturating with baryta-water, and again agitating with ether. On removing the ether by distillation, there remains a syrupy residue which soon crystallises and may be further purified by redistillation. The treatment with baryta may be dispensed with by repeatedly distilling with the thermometer, and collecting only those portions which pass over between 269° and 272°.

Resorcin is very soluble in *water*, *alcohol*, and *ether*, insoluble in sulphide of carbon, and in chloroform. It crystallises only from very concentrated solutions, in tabular crystals or short thick prisms belonging, like orcin, to the trimetric system. When recently prepared it is quite colourless, but acquires a faint reddish tint by keeping or by exposure to the air. It melts at 99°, and begins to volatilise at a slightly higher temperature; boils at 271°, and distils almost without residue; burns with a bright flame. It has a neutral reaction and a strong unpleasant, sweet, and somewhat irritating taste. It gives by analysis 65·1 and 65·5 per cent. carbon and 5·7 hydrogen, the formula requiring 65·5 C and 5·5 H. Vapour-density, obs. = 4·1; calc. = 3·8 (the residue in the globe was dark brown, the substance having been partly decomposed by the high temperature required).

The aqueous solution forms with *ferric chloride* a dark violet-coloured liquid, which on addition of ammonia deposits ferric oxide and becomes colourless. *Chloride of lime* produces a violet colour not very permanent. The solution mixed with *ammonia* and exposed to the air, becomes rose-red, afterwards darker, and ultimately brownish. The ammoniacal solution, evaporated at a gentle heat, dries up to a dark blue mass, which redissolves in water with blue colour, and is reddened by acids. Resorcin reduces *nitrate of silver* at the boiling heat, on addition of ammonia. Heated with an alkaline *cupric* solution, it throws down cuprous oxide.

*Tribromo-resorcin*, $C^{6}H^{3}Br^{3}O^{2}$, is precipitated on adding bromine-water to an aqueous solution of resorcin, in small, bulky, interlaced needles, sparingly soluble in cold water, more easily in boiling water, also in alcohol.

**ORELLIN.** A yellow colouring matter contained, together with bixin (i. 600), in annotto. It is soluble in water and in alcohol, slightly soluble in ether, and dyes alumed goods yellow. (Chevreul.)

**OREOSELIN.** $C^{7}H^{6}O^{2}$.—A substance isomeric with benzoic acid, obtained: 1. By treating hydrochlorate of athamantin with boiling water; sometimes, however, this process yields oreoselone (Schnedermann and Winckler, Ann. Ch. Pharm. li. 315).—2. By the action of alcoholic potash on peucedanin (Wagner, J. pr. Chem. lxii. 275):

$$\underset{\text{Peucedanin.}}{C^{12}H^{12}O^{3}} + KHO = \underset{\text{Oreoselin.}}{C^{7}H^{6}O^{2}} + \underset{\text{Angelate of potassium.}}{C^{5}H^{7}KO^{2}}.$$

It crystallises in fine silky needles, slightly soluble in cold water, very soluble in alcohol and ether, also with yellow colour in dilute potash; less easily in ammonia, the solution yielding a yellow precipitate with acetate of lead.

**OREOSELONE.** $C^{14}H^{10}O^{3}$.—This body, the anhydride of oreoselin ($2C^{7}H^{6}O^{2} - H^{2}O = C^{14}H^{10}O^{3}$), is produced by the decomposition of athamantin (Schnedermann and Winckler, *loc. cit.*):

$$\underset{\text{Athamantin.}}{C^{24}H^{30}O^{7}} = \underset{\text{Oreoselone.}}{C^{14}H^{10}O^{3}} + \underset{\text{Valerianic acid.}}{2C^{5}H^{10}O^{2}}$$

To prepare it, hydrochloric acid gas is passed over dry athamantin till complete liquefaction takes place; the mass is heated to expel valerianic acid; and the amorphous porous mass obtained on cooling is purified by crystallisation from boiling alcohol, in which, however, it is but slightly soluble.

Oreoselone crystallises in nodules or cauliflower-like masses composed of fine needles grouped concentrically. It is tasteless and inodorous, insoluble in water; alkalis dissolve it, forming red solutions from which acids precipitate it slightly modified. It melts at 190° to a clear liquid, which carbonises at a higher temperature.

**ORGANIC ANALYSIS.** See ANALYSIS, ORGANIC (i. 225).

**ORGANIC CHEMISTRY.** The peculiar character of the chemical compounds formed in the bodies of plants and animals, and the failure of the earlier attempts to produce them by artificial means, led to the erroneous idea that their formation was due to a mysterious power called "vital force," supposed to reside in the living organism, and to govern all the changes and processes taking place within it. In accordance with this idea, the chemistry of organic compounds, including those which were formed by artificial processes from the products of vegetable and animal life, was erected into a special branch of chemical science.

Later researches have however shown that a large number of compounds, formerly regarded as producible only under the influence of the so-called vital force, may be formed either by direct combination of their elements, or by chemical transformation of inorganic compounds.

The first step in the formation of organic compounds from their elements, was made by Wöhler, who showed in 1828 that urea can be produced by molecular transformation of cyanate of ammonium. This experiment, viewed in conjunction with the fact subsequently established by Fownes in 1841, that cyanogen can be formed by direct combination of its elements (ii. 198), is conclusive of the possibility of forming a product of the living organism from inorganic materials. At the time of Wöhler's discovery, however, cyanogen had not been obtained, excepting from substances originally derived from the vegetable or animal organism, and accordingly the idea of the peculiar nature of organic compounds, as essentially products of life, still maintained its ground. Even in the first volume of Gmelin's Organic Chemistry (published in 1848) we find it stated that "the bodies of the organic kingdom are distinguished from those of the inorganic kingdom by their inherent vital force," although in the course of the same volume, several instances are mentioned of the formation of organic compounds from inorganic materials, viz.:—1. The formation of cyanogen, as above mentioned, by passing nitrogen gas over a mixture of charcoal and potassic carbonate; also that of cyanide of ammonium by heating a mixture of sal-ammoniac, plumbago and lime or oxide of lead;—2. The formation of oily and mould-like compounds by the action of acids on carburetted iron;—3. The formation of the acid $CHCl^{3}SO^{3}$ from the compound $CCl^{4}SO^{2}$ (itself produced by the action of chlorine and water on sulphide of carbon, i. 776), and its conversion into $CH^{4}SO^{3}$ by the action of reducing agents.—4. The formation of tetrachloride of carbon, $CCl^{4}$, by the action of chlorine on disulphide of carbon; the conversion of the tetrachloride into the dichloride, $C^{2}Cl^{4}$, by passing it through a red-hot tube; the formation of trichloracetic acid (i. 877) from the last-mentioned compound, by the action of chlorine and water in sunshine; and the conversion of the trichloracetic into acetic acid, by the action of reducing agents.—5. The formation of sulphocyanate of ammonium by the action of ammonia on sulphide of carbon.—6. The formation of rhodizonic, croconic and oxalic acids, together with mould-like substances, in the ordinary process of preparing potassium. Gmelin observes, however, that on the whole it appears that only the lower order of organic compounds, namely those which contain but few atoms of carbon, can be formed artificially from inorganic materials, excepting perhaps the mould-like substances; and he further expresses a doubt whether all carbon compounds, even sulphide of carbon, carbonic oxide and carbonic acid, ought not to be regarded as organic.

The question of the formation of organic compounds from their elements has however been completely set at rest by the classic researches of Berthelot, who showed in 1856 that formate of potassium is produced by the direct union of carbonic oxide with hydrate of potassium (iii. 683), and subsequently that acetylene may be formed by the direct combination of carbon with hydrogen, and that marsh-gas, ethylene, and several of its homologues may likewise be formed from inorganic materials (see HYDROCARBONS, iii. 188). These hydrocarbons may be converted into alcohols, *e. g.* marsh-gas into methylic alcohol (iii. 988), and ethylene into ethylic alcohol (i. 72); and from the alcohols, by well-known processes, a large number of other compounds may be obtained, namely aldehydes, acids, acetones, ethers, amines, organo-metallic bodies, &c.

Another kind of chemical transformation, formerly supposed to be peculiarly a function of the living organism, is the formation of compounds containing a greater number of carbon-atoms from others containing a smaller number. In the earlier days of organic chemistry, indeed, the principal agent of transformation known was oxidation, by which an organic body is for the most part lowered in the scale, its carbon and hydrogen being gradually burnt away, until at length the whole is resolved into carbonic anhydride and water, together with ammonia if nitrogen is also present. The possibility of effecting the opposite kind of transformation, of building up organic compounds from others lower in the scale—that is containing a smaller number of atoms of carbon or hydrogen, or both—has however been demonstrated in a great number of instances. Thus it has been known for some years that naphthalene, $C^{10}H^8$, may be formed by passing the vapour of alcohol or ether, or the vapours evolved by the dry distillation of benzoate of calcium, through a red-hot tube. Other instances of the building up of organic compounds from others of lower order are the production of potassic oxalate from the formate, by heating with potash-lime ($2CHKO^2 = C^2K^2O^4 + H^2$); the formation of decatylene, $C^{10}H^{20}$, and many other of the higher olefines by distilling amylic alcohol, $C^5H^{12}O$, with phosphoric anhydride or chloride of zinc; the conversion of urea by heat into cyanuric acid; of sulphobenzene, $C^7H^{10}S$, by dry distillation into stilbene, $C^{14}H^{12}$, &c. &c. (see *Gmelin's Handbook*, vii. 43). Of far greater importance, however, than these isolated instances of the accumulation of carbon-atoms by artificial means, are the general methods which have been discovered of building up the terms of homologous series—especially that discovered by Mendius, namely the conversion of the cyanide of an alcohol-radicle into the amine of the radicle next higher in the series, *e. g.* cyanide of hydrogen into methylamine, cyanide of methyl into ethylamine, &c. (see HOMOLOGOUS SUBSTANCES, iii. 164).

Since then the simpler organic compounds can be formed from inorganic materials, and from these a large number of the more complex compounds can be synthetically produced, it seems not improbable that all the proximate principles of the vegetable and animal organisms will ultimately be formed from their elements by artificial means. The notion of organic compounds as constituting a class essentially distinct from inorganic or mineral compounds in their formation and constitution, must therefore be abandoned. Still the marked peculiarities of character by which bodies of vegetable and animal origin, and those formed from them, are for the most part distinguished from those of purely mineral origin, especially their more complex constitution and ready decomposibility, as exhibited in their behaviour when heated, and by the phenomena of fermentation and putrefaction, have led to various attempts to define organic compounds in a more satisfactory manner. Thus Liebig formerly defined Organic Chemistry as the "Chemistry of Compound Radicles." Such a definition, however, cannot be maintained at the present day, when almost every class of salts, of mineral as well as of organic origin, is supposed to contain a compound radicle, *e.g.* $NO^2$ in the nitrates, $SO^2$ in the sulphates, &c. Gmelin in his "Handbook" defines organic chemistry as the "Chemistry of carbon-compounds containing more than 1 atom of carbon" ($C=6$). This definition excludes the simple carbon-compounds, $CO$, $CO^2$, $CS^2$, which are usually regarded as inorganic. It is impossible, however, to draw any precise line of demarcation, with regard to properties and mode of formation, between these bodies and others, such as acetylene and marsh-gas, which this definition would include among organic compounds: indeed Gmelin himself, as already observed, suggests the propriety of considering all compounds containing carbon as organic. Such is in fact the conclusion at which we must ultimately arrive respecting the meaning of the term Organic Chemistry, namely that it signifies the Chemistry of Carbon-compounds; and in this sense it is used by Gerhardt in his *Traité de Chemie organique*, and by Kekulé in his *Lehrbuch der Organischen Chemie.*

The study of the chemical processes which take place in the bodies of living plants and animals, and of the composition and properties of the complex fluids and organs of those bodies, is the province of Physiological Chemistry, a branch of the science which bears the same relation to organic chemistry, or the chemistry of carbon-compounds, that chemical geology bears to mineral chemistry.

**ORGANO-METALLIC BODIES.** This term is applied to a numerous class of compounds in which an organic radicle such as ethyl is *directly* combined with a metal, and serves to distinguish them from other organic compounds containing metals, but in which the metal is *indirectly* united or linked, as it were, to the metal by diatomic oxygen. Although organo-metallic bodies, constituted according to this definition, are, with one exception, the creation of the last sixteen years, yet their derivatives have been known for a much longer period. From the time that an organic acid was first united with a metallic base, these organic compounds containing metals indirectly united date their existence. It is true that these derivatives have not been regarded from this point of view; but a little consideration will serve to show that they stand in the same relation to organo-metallic bodies in the strict sense of the term, as the ethers, alcohols, acids, and numerous other organic families occupy with regard to the alcohol-radicles from which they are derived. Thus the organo-metallic compound zinc-ethyl yields by oxidation ethylate of zinc;—

$$\underset{\text{Zincethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + O^2 = \underset{\text{Ethylate of zinc.}}{Zn''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.}$$

a body which, although unknown until formed by this reaction, has undoubted and well-known analogues in the ethylates of potassium and sodium.

By suitable processes of oxidation, ethylate of zinc may be converted into acetate of zinc.

$$\underset{\text{Ethylate of zinc.}}{Zn''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.} + O^4 = \underset{\text{Acetate of zinc.}}{Zn''\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.} + 2H^2O.$$

The ethyl-compounds of potassium and sodium also pass through analogous phases of oxidation.

Again potassium-ethyl and sodium-ethyl, under the influence of carbonic acid, yield the propionates of potassium and sodium:

$$\underset{\text{Potassium-ethyl.}}{KC^2H^5} + CO^2 = \underset{\text{Propionate of potassium.}}{KOC^3H^5O.}$$

The same result may also probably be reached by two distinct stages, viz., first by the conversion of potassium-ethyl and sodium-ethyl into the ethylates of potassium and sodium:

$$\underset{\text{Potassium-ethyl.}}{KC^2H^5} + O = \underset{\text{Ethylate of potassium.}}{KOC^2H^5}$$

and secondly by the action of carbonic oxide upon these bodies:

$$\underset{\text{Ethylate of potassium.}}{KOC^2H^5} + CO = \underset{\text{Propionate of potassium.}}{KOC^3H^5O.}$$

The second stage of this conversion has not yet been experimentally realised, but Berthelot's production of formate of potassium from carbonic oxide and hydrate of potassium exhibits a homologous reaction.

These examples serve to point out the relations existing between organo-metallic bodies in the usual acceptation of the term, and that far more numerous class of derivatives to which the same name might without impropriety be applied; but it is scarcely necessary to remark that the present article will be confined to the consideration of organo-metallic bodies in the usual and more restricted sense of the term.

### FORMATION OF ORGANO-METALLIC BODIES.

Organo-metallic bodies can be produced by a great variety of processes; but these numerous methods of formation, with very few exceptions, admit of being grouped under four heads.

1. *Formation by union of the Organic Radicle in statu nascenti with the metal, or by the coalescence of the latter with the iodide of the Organic Radicle.*

By this method, the organic radicle is almost invariably presented to the metal in the form of iodide,—a state of combination surpassing all others in the facility with which the two components separate under the influence of chemical affinity. The metal, made to present as large a surface as possible by granulation or otherwise, is placed in contact with the organic iodide and heated in a close vessel of adequate strength to resist the pressure of the vapours and gases generated.

For a figure and description of the apparatus see BATH (i. 521).

In some cases the agency of light may be advantageously employed to replace that of heat as in the formation of organo-tin compounds, whilst in the case of mercurial compounds, solar radiation is almost essentially necessary. Where light is employed, the materials are enclosed in glass vessels which are then exposed either to diffuse daylight, direct sunlight, or to the solar rays concentrated by a parabolic reflector. In the latter case the vessel may be surrounded by water or by a solution of sulphate of copper to absorb the calorific rays.

The organic compounds of zinc, cadmium, magnesium, aluminium and glucinum are produced by the thermal process, those of tin may be formed either by the thermal or by the light process, whilst the organo-compounds of mercury can only be generated in the class of process now under discussion by luminiferous agency. The thermal method of procedure is well illustrated in the preparation of *zincethyl*.

The reaction which occurs on heating zinc and iodide of ethyl is usually expressed by the following equation:

$$\underset{\text{Iodide of ethyl.}}{2\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}} \quad + \quad 2Zn'' \quad = \quad \underset{\text{Zinc-ethyl.}}{\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\}Zn''} \quad + \quad Zn''\left\{\begin{matrix}I\\ I\end{matrix}\right.$$

The actual chemical changes occurring in the formation of zincethyl are, however, by no means so simple. This body is found in a free state, in very small quantity only, amongst the products of the reaction of zinc upon iodide of ethyl, but there exists amongst these products a crystalline body which contains zinc, ethyl, and iodine, and may be regarded as formed according to the equation:

$$\underset{\text{Iodide of ethyl.}}{C^2H^5I} \quad + \quad Zn \quad = \quad \underset{\text{Ethiodide of zinc.}}{Zn''(C^2H^5)I.}$$

This compound is decomposed at about 150°, yielding iodide of zinc and zincethyl:

$$\underset{\text{Ethiodide of zinc.}}{2Zn''(C^2H^5)I} \quad = \quad \underset{\text{Zincethyl.}}{Zn''(C^2H^5)^2} \quad + \quad Zn''I^2.$$

Contemporaneously with the first of the above reactions, there occur others in which ethyl, hydride of ethyl, and ethylene are produced. The separation of ethyl in this reaction is doubtless due to the direct action of zinc upon iodide of ethyl:

$$\underset{\text{Iodide of ethyl.}}{2(C^2H^5)I} \quad + \quad Zn \quad = \quad \underset{\text{Ethyl.}}{(C^2H^5)^2} \quad + \quad Zn''I^2$$

whilst the appearance of the secondary products, ethylene and hydride of ethyl, results from the action of the ethiodide of zinc upon iodide of ethyl:

$$\underset{\text{Ethiodide of zinc.}}{Zn''(C^2H^5)I} \quad + \quad \underset{\text{Iodide of ethyl.}}{C^2H^5I} \quad = \quad \underset{\text{Hydride of ethyl.}}{C^2H^5.H} \quad + \quad \underset{\text{Ethylene.}}{C^2H^4} \quad + \quad Zn''I^2.$$

Notwithstanding, however, the intermediate formation of ethiodide of zinc, in the manner above indicated, the final result of the reaction is correctly expressed in the first of the above equations.

The reactions by which ethyl, hydride of ethyl, and ethylene are produced can be almost completely avoided by the admixture of an equal volume of anhydrous ether with the iodide of ethyl. The yield of zincethyl is thus proportionately increased.

*Zinc-methyl* and *zinc-amyl* may be also thus produced, but they are obtained in a state of purity with extreme difficulty, and are therefore more advantageously prepared according to the fourth method of formation. No attempt has yet been made to form the corresponding compounds of the remaining alcohol-radicles.

*Organo-compounds of Tin.*—Although these bodies can be obtained by other processes, the general method we are now considering is doubtless the most convenient mode of producing most of them. Tin is capable of forming three distinct classes of binary inorganic compounds which may be represented by the following general formulæ:

$$Sn''\left\{\begin{matrix}R\\ R\end{matrix}\right. \qquad\qquad 2\left(Sn'''\left\{\begin{matrix}R\\ R\\ R\end{matrix}\right.\right) \qquad\qquad Sn^{iv}\left\{\begin{matrix}R\\ R\\ R\\ R\end{matrix}\right.$$

This threefold atomic character of the metal renders the result of its action upon the iodides of the alcohol-radicles considerably less simple than that of zinc. Without taking into account compounds to which a still more complex constitution has been assigned, the existence of the following series of organo-metallic bodies containing tin has been established: *

$$\underset{}{\overset{\textbf{1st Series.}}{Sn''\left\{\begin{matrix}R+\\ R+\end{matrix}\right.}} \qquad\qquad \overset{\textbf{2nd Series.}}{2\left(Sn'''\left\{\begin{matrix}R+\\ R+\\ R+\end{matrix}\right.\right)} \qquad\qquad \overset{\textbf{3rd Series.}}{2\left(Sn'''\left\{\begin{matrix}R+\\ R+\\ R-\end{matrix}\right.\right)}$$

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[*] In these formulæ R+ represents a positive organic radicle, and R− a negative radicle: no negative organic radicle as such, has yet been introduced into these compounds.

$$\underset{}{\overset{\text{4th Series.}}{Sn^{iv}\left\{\begin{matrix}R+\\R+\\R+\\R+\end{matrix}\right.}}\qquad\qquad \overset{\text{5th Series.}}{Sn^{iv}\left\{\begin{matrix}R+\\R+\\R+\\R-\end{matrix}\right.}\qquad\qquad \overset{\text{6th Series.}}{Sn^{iv}\left\{\begin{matrix}R+\\R+\\R-\\R-\end{matrix}\right.}$$

The second and fourth of these series have not yet been produced by the method we are now considering.

First Series. *Stannous ethide* $\left(Sn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.\right)$ is produced in small quantities by the action of heat upon a mixture of iodide of ethyl and tin:

$$\underset{\text{Iodide of ethyl.}}{2(C^2H^5)I} \quad + \quad Sn^2 \quad = \quad \underset{\text{Stannous ethide.}}{Sn''(C^2H^5)^2} \quad + \quad Sn''I^2.$$

*Stannous methide* is doubtless formed under similar conditions.

The third Series of stann-organic compounds is formed by reactions, of which the following may be regarded as a type:

$$\underset{\substack{\text{Iodide of}\\\text{methyl.}}}{4(CH^3)I} \quad + \quad Sn^3 \quad = \quad \underset{\substack{\text{Dimethiodide}\\\text{of tin.}}}{2[Sn'''(CH^3)^2I]} \quad + \quad SnI^2.$$

Fifth Series.—The following chemical change expresses the mode of formation of compounds belonging to this series:

$$\underset{\substack{\text{Iodide of}\\\text{methyl.}}}{3(CH^3)I} \quad + \quad Sn^2 \quad = \quad \underset{\substack{\text{Stannic iodo-}\\\text{trimethide.}}}{Sn^{iv}(CH^3)^3I} \quad + \quad Sn''I^2.$$

Sixth Series.—The most abundant products of the action of tin upon the iodides of the alcohol-radicles belong to this series; indeed, if the action be produced by light instead of heat, they are formed almost to the complete exclusion of the others. It is necessary, however, to remark that the materials exposed to light should be completely excluded from atmospheric oxygen, otherwise the liquid assumes an orange colour, and the action is so effectually arrested that an exposure for several months to sunlight, concentrated by a parabolic mirror, will scarcely produce any appreciable change. The following reaction explains the formation of bodies belonging to this series:

$$\underset{\substack{\text{Iodide of}\\\text{methyl.}}}{2(CH^3)I} \quad + \quad Sn \quad = \quad \underset{\substack{\text{Stannic}\\\text{dimethiodide.}}}{Sn^{iv}(CH^3)^2I^2}.$$

It is evident that three series of tin-compounds are still wanting to complete the category, viz.:

$$Sn''\left\{\begin{matrix}R+\\R-\end{matrix}\right.\qquad Sn^{iv}\left\{\begin{matrix}R+\\R-\\R-\\R-\end{matrix}\right.\qquad 2\left(Sn'''\left\{\begin{matrix}R+\\R-\\R-\end{matrix}\right.\right)$$

It is somewhat remarkable that no organo-tin compounds containing only one equivalent of positive radicle, have hitherto been produced. The inference to be drawn from this, that such bodies do not exist, must be checked by the fact that no special attempts have yet been made to form them.

*Organo-compounds of Mercury.*—The reaction of mercury upon the iodides of the alcohol-radicles gives rise to two series of organic compounds, the general formulæ of which may thus be written:

$$\overset{\text{1st Series.}}{Hg''\left\{\begin{matrix}R+\\R-\end{matrix}\right.}\qquad\qquad\qquad \overset{\text{2nd Series.}}{Hg''\left\{\begin{matrix}R+\\R+\end{matrix}\right.}$$

The first series only of these bodies can be produced by the general mode of formation now under consideration; but the members of the second series are readily obtained by the action of an organo-zinc compound upon those of the first.

For the production of the first series of these bodies, the action of light is essential (except in the case of mercuric iodo-allide), no elevation of temperature being capable of producing the chemical change. The following equation sufficiently exhibits the nature of the reaction:

$$\underset{\substack{\text{Iodide of}\\\text{methyl.}}}{CH^3I} \quad + \quad Hg \quad = \quad \underset{\substack{\text{Mercuric}\\\text{iodomethide.}}}{Hg''(CH^3)I}.$$

For the production of the methyl-compound, bright sunlight may be employed; but the reaction for the ethyl-body must be conducted in diffused daylight only, otherwise no organo-metallic compound will be produced, the ethyl being eliminated chiefly as such, but partly, also, as hydride of ethyl and ethylene:

$$\underset{\text{Iodide of ethyl.}}{2(C^2H^5)I} + Hg = Hg''I^2 + \underset{\text{Ethyl.}}{C^2H^5.C^2H^5}.$$

$$\underset{\text{Iodide of ethyl.}}{2(C^2H^5)I} + Hg = Hg''I^2 + \underset{\text{Hydride of ethyl.}}{C^2H^5.H} + \underset{\text{Ethylene.}}{C^2H^4}.$$

In addition to these bodies, compounds containing arsenic and antimony can also be produced by this general mode of formation; but they are obtained with greater facility by the second method, which will now be described.

### 2. *Formation of Organo-metallic bodies by the action of the respective Metals alloyed with Potassium or Sodium upon the Iodides of the Alcohol-radicles.*

The principles involved in this second general mode of production are essentially similar to those in the first, but there is here less tendency to form compounds containing negative as well as positive radicles. The simultaneous production of an organo-potassium or sodium compound need not be feared, since such compounds cannot exist in the presence of the iodides of the alcohol-radicles.

This mode of formation will be sufficiently illustrated by the following reactions:

#### *Arsenic-compounds.*

$$\underset{\text{Iodide of methyl.}}{4(CH^3)I} + 2(As'''Na^3) = \underset{\text{Cacodyl.}}{2(As'''(CH^3)^2)} + 4NaI.$$

$$\underset{\text{Iodide of methyl.}}{3(CH^3)I} + As'''Na^3 = \underset{\text{Trimethylarsine.}}{As'''(CH^3)^3} + 3NaI.$$

$$\underset{\text{Iodide of methyl.}}{4(CH^3)I} + As'''Na^3 = \underset{\text{Iodide of tetramethylarsonium.}}{As^{v}(CH^3)^4I} + 3NaI.$$

#### *Antimony-compounds.*

$$\underset{\text{Iodide of methyl.}}{3(CH^3)I} + Sb''Na^3 = \underset{\text{Trimethylstibine.}}{Sb'''(CH^3)^3} + 3NaI.$$

$$\underset{\text{Iodide of methyl.}}{4(CH^3)I} + Sb'''Na^3 = \underset{\text{Iodide of tetramethylstibonium.}}{Sb^{v}(CH^3)^4I} + 3NaI.$$

#### *Tin-compounds.*

$$\underset{\text{Iodide of methyl.}}{2(CH^3)I} + Sn''Na^2 = \underset{\text{Stannous-methide.}}{Sn''(CH^3)^2} + 2NaI.$$

$$\underset{\text{Iodide of methyl.}}{6(CH^3)I} + 2(Sn''Na^2) = \underset{\text{Stann-sesqui-methide.}}{2[Sn'''(CH^3)^3]} + 6NaI.$$

$$\underset{\text{Iodide of methyl.}}{4(CH^3)I} + Sn^{iv}Na^4 = \underset{\text{Stannic methide.}}{Sn^{iv}(CH^3)^4} + 4NaI.$$

#### *Mercury-compounds.*

When the iodides of the alcohol radicles are placed in contact with sodium-amalgam, no perceptible action takes place at ordinary temperatures, even after prolonged digestion, but on the addition of a few drops of acetic ether, the amalgam is immediately attacked and a brisk action with considerable elevation of temperature attends the formation of the organo-mercurial compound. The function of the acetic ether in this reaction is not understood, but the ether is found in undiminished quantity at the close of the reaction. The following equation illustrates the formation of these compounds:

$$\underset{\text{Iodide of methyl.}}{2(CH^3)I} + Na^2Hg'' = \underset{\text{Mercuric methide.}}{Hg''(CH^3)^2} + 2NaI.$$

#### *Lead-compound.*

$$\underset{\text{Iodide of ethyl.}}{6(C^2H^5)I} + 2(Pb'''Na^3) = \underset{\text{Plumb-triethide.}}{2[Pb'''(C^2H^5)^3]} + 6NaI.$$

### *Bismuth-compound.*

$$\underset{\text{Iodide of ethyl.}}{3(C^2H^5)I} + Bi'''Na^3 = \underset{\text{Bis-triethide.}}{Bi'''(C^2H^5)^3} + 3NaI.$$

### *Tellurium-compounds.*

Organo-tellurium compounds are formed by a modification of this method, which consists in distilling telluride of potassium with ethylsulphate of potassium and its homologues:

$$\underset{\text{Methylsulphate of potassium.}}{2(S^{vi}O^2.CH^3O.KO)} + To''K^2 = \underset{\text{Tellurium-methyl.}}{Te''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.} + \underset{\text{Sulphate of potassium.}}{2(S^{vi}O^2(KO)^2)}.$$

The ethyl and amyl compounds are prepared by homologous reactions.

3. *Formation of Organo-metallic bodies by the action of the Zinc-compounds of the Organic Radicles upon the Haloïd compounds either of the Metals themselves or of their Organo-derivatives.*

For the production of organo-metallic bodies containing less positive metals than zinc, this method is perhaps not only the most convenient, but also capable of the most general application. Compounds containing mercury, tin, lead, antimony, and arsenic have been thus produced, but it has failed when applied to the haloïd compounds of copper, silver, and platinum, for although these bodies are violently acted upon, the organic group does not unite with the metal.

The following reactions illustrate this method of formation:—

### *Mercury-compounds.*

$$\underset{\text{Zinc-methyl.}}{Zn''(CH^3)^2} + Hg''Cl^2 = \underset{\text{Mercuric methide.}}{Hg''(CH^3)^2} + Zn''Cl^2.$$

$$\underset{\text{Zinc-methyl.}}{Zn''(CH^3)^2} + 2Hg''Cl^2 = \underset{\text{Mercuric chloromethide.}}{2Hg''(CH^3)Cl} + Zn''Cl^2.$$

Mercurous ethide and mercurous methide have not yet been obtained either by this or any other process. The instability of mercurous compounds, as seen in the inorganic oxide and iodide, is brought to a climax in organic mercurous compounds; the latter are instantly transformed into metallic mercury and the more stable organo-mercuric compounds. Thus, when zinc-ethyl acts upon mercurous chloride, the following change results:—

$$\underset{\text{Zinc-ethyl.}}{Zn''(C^2H^5)^2} + 2HgCl = \underset{\text{Mercuric ethide.}}{Hg''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + Hg + Zn''Cl^2.$$

### *Tin-compounds.*

$$\underset{\text{Zinc-ethyl.}}{2Zn''(C^2H^5)^2} + \underset{\text{Stannic chloride.}}{Sn^{iv}Cl^4} = \underset{\text{Stannic ethide.}}{Sn^{iv}(C^2H^5)^4} + 2Zn''Cl^2.$$

$$\underset{\text{Zinc-ethyl.}}{Zn^{4}(C^2H^5)^2} + \underset{\text{Stannic diethiodide.}}{Sn^{iv}(C^2H^5)^2I^2} = \underset{\text{Stannic ethide.}}{Sn^{iv}(C^2H^5)^4} + Zn''I^2.$$

$$\underset{\text{Zinc-ethyl.}}{3Zn''(C^2H^5)^2} + 2Sn^{iv}Cl^4 = \underset{\text{Chlorotriethide of tin.}}{2Sn^{iv}(C^2H^5)^3Cl} + 3Zn''Cl^2.$$

$$\underset{\text{Zinc-ethyl.}}{Zn''(C^2H^5)^2} + Sn^{iv}Cl^4 = \underset{\text{Stannic dichlorethide.}}{Sn^{iv}(C^2H^5)^2Cl^2} + Zn''Cl^2.$$

### *Lead-compound.*

The following is the only reaction which has hitherto been effected by the method which we are now considering:—

$$\underset{\text{Zinc-ethyl.}}{2Zn''(C^2H^5)^2} + 2Pb''Cl^2 = \underset{\text{Plumbic ethide.}}{Pb^{iv}(C^2H^5)^4} + Pb + 2Zn''Cl^2.$$

### *Antimony-compounds.*

$$\underset{\text{Zinc-methyl.}}{3Zn''(CH^3)^2} + 2Sb'''Cl^3 = \underset{\text{Trimethylstibine.}}{2Sb'''(CH^3)^3} + 3Zn''Cl^2.$$

### *Arsenic-compounds.*

$$\underset{\text{Zinc-methyl.}}{3Zn''(CH^3)^2} + 2As'''Cl^3 = \underset{\text{Trimethylarsine.}}{2As'''(CH^3)^3} + 3Zn''Cl^2.$$

### 4. *Formation of Organo-metallic bodies by the displacement of a Metal in an Organo-metallic compound by another and more positive Metal.*

This fourth mode of producing organo-metallic bodies has been successfully applied to the formation of the compounds of sodium, potassium, lithium, aluminium, and zinc. In the case of the three first-named metals the reaction takes place at ordinary temperatures, the original body operated upon being an organo-zinc compound which also enters the composition of the resulting organo-potassium, sodium, or lithium compound as shown in the following reactions:—

$$\underset{\text{Zinc-ethyl.}}{3Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} \quad + \quad Na^2 \quad = \quad \underset{\text{Sodio-zinc-ethyl.}}{2\begin{matrix}Zn''\\Na\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.} \quad + \quad Zn.$$

$$\underset{\text{Zinc-ethyl.}}{3Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} \quad + \quad K^2 \quad = \quad \underset{\text{Potassio-zinc-ethyl.}}{2\begin{matrix}Zn''\\K\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.} \quad + \quad Zn.$$

Sodium also displaces mercury from mercuric ethide; sodium-ethyl is probably formed, but the exact nature of the reaction has not been ascertained.

The organo-zinc compounds are obtained by the action of granulated zinc upon the corresponding mercury compounds at a temperature varying from 100° to 130° C. The following example shows the nature of this transformation.

$$Hg''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right. \quad + \quad 2Zn \quad = \quad Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right. \quad + \quad Zn''Hg''.$$

The first mode of formation above described, cannot, without formidable difficulties, be applied to the production of zinc-methyl and zinc-amyl in a state of purity, but by the fourth method, now under consideration, these bodies are obtained with great facility; for the preparation of zinc-ethyl, however, the first method is the most advantageous.

### PROPERTIES OF ORGANO-METALLIC BODIES.

The organo-metallic compounds as a class are distinguished by the extraordinary energy of their affinities. With certain exceptions, presently to be noticed, their disposition to unite with negative elements increases with the positive character of the metal and with the smallness of the atomic weight of the alcohol-radicle. Thus organo-potassium and sodium compounds possess more chemical energy than those of zinc, whilst the latter are more active than the compounds of arsenic, antimony, tin, or lead. Again, in the series belonging to each metal, the methylic compounds are more energetic than the ethylic ones, whilst the last greatly surpass the amylic compounds in this respect. But whilst these general principles govern the chemical energy of organo-metallic bodies, their effect is modified by the degree of saturation in which the metal exists. Although this circumstance has hitherto received only partial elucidation, yet we have evidence of its effects in the case of organo-tin compounds. Both stannous ethide and stannous methide combine directly with atmospheric oxygen, and the union takes place with tolerable rapidity; but neither stannic ethide nor stannic methide is in the least degree acted upon by free oxygen at ordinary temperatures; even iodine acts upon them with difficulty. This diminution of chemical energy in organo-stannic compounds cannot be ascribed to the mere influence of the additional weight of hydrocarbon which they contain, since stannous amylide readily unites with free oxygen at ordinary temperatures, although the single atom of amyl which it contains is considerably heavier than the double atom of either methyl or ethyl present in the organo-stannic compounds just cited.

Organo-metallic compounds in a state of partial saturation play the part of compound radicles. They are monatomic, diatomic, triatomic, or tetratomic, according to the number of atoms requisite to complete their saturation. On the other hand, organo-metallic bodies in a state of saturation never perform radicle functions: they never undergo chemical change without decomposition. Thus zinc-ethyl, stannic ethide, mercuric ethide, and plumbic ethide all give substitution-products when they are chemically acted upon.

*Potassium, sodium, and lithium series.*[*]—These bodies have not yet been isolated; they are known only in combination with the corresponding zinc or mercury compounds. The double compound of sodium-ethyl and zinc-ethyl is the only one which has hitherto been submitted to analysis. Its formula is $\left.\begin{matrix}Zn''\\Na\end{matrix}\right\}(C^2H^5)^3$.

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[*] Wanklyn, Proc. Roy. Soc. iv. 341. Frankland, Proceedings of the Royal Institution, vol. iv.

This compound first separates from its solution in zinc-ethyl as a transparent fluid, which after some time solidifies to a mass of large tabular crystals, fusing at 27° C, but when once fused remaining fluid at several degrees below that point. On the application of a moderate heat to this compound, gases are evolved, and a mixture of sodium and zinc without carbon is left behind. Sodio-zinc ethyl decomposes water with great violence, forming hydride of ethyl, and the hydrated oxides of zinc and sodium. The behaviour with negative elements has not yet been studied. Its most interesting reaction consists in the absorption of carbonic anhydride, which it transforms into propionic acid. The sodium-ethyl alone takes part in this reaction:*

$$\underset{\text{Sodium-ethyl.}}{NaC^2H^5} + CO^2 = \underset{\text{Propionate of sodium.}}{\left.\begin{matrix}C^3H^5O\\Na\end{matrix}\right\}O.}$$

No compound of any of these bodies with a negative element has been obtained. Their action upon carbonic anhydride proves that they possess a still higher reducing power than the corresponding organo-zinc compounds, and they will therefore doubtless prove valuable agents for the substitution of positive groups for negative elements in cases where organo-zinc compounds fail to produce the desired effect.

Sodium-ethyl decomposes the iodides of the alcohol-radicles in the cold, with formation of iodide of sodium.†

$$\underset{\text{Sodium-ethyl.}}{NaC^2H^5} + \underset{\text{Iodide of ethyl.}}{\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}} = NaI. + \underset{\text{Hydride of ethyl.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}} + \underset{\text{Ethylene.}}{C^2H^4.}$$

Owing to this behaviour, potassium and sodium compounds can only be prepared by method No. 4.

The following bodies belonging to this series have been described:

| | | | |
|---|---|---|---|
| Potassio-zinc methyl . | $\begin{matrix}Zn''\\K'\end{matrix}\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.$ | Lithio-mercuric methide | $\begin{matrix}Hg''\\Li'\end{matrix}\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.$ |
| Potassio-zinc ethyl . . | $\begin{matrix}Zn''\\K'\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$ | Lithio-mercuric ethide . | $\begin{matrix}Hg''\\Li'\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$ |
| Sodio-zinc methyl . . | $\begin{matrix}Zn''\\Na'\end{matrix}\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.$ | Lithio-zinc methide . | $\begin{matrix}Zn'\\Li'\end{matrix}\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.$ |
| Sodio-zinc ethyl . . | $\begin{matrix}Zn''\\Na'\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$ | Lithio-zinc ethide . . | $\begin{matrix}Zn''\\Li'\end{matrix}\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$ |

*Magnesium series.*‡—The compounds containing ethyl and methyl only have hitherto been examined, and the former alone submitted to analysis. These bodies possess a close similarity to organo-zinc compounds. They are very volatile colourless liquids, possessing a powerful alliaceous odour; are spontaneously inflammable, and decompose water with violence. They do not readily decompose the iodides of the alcohol-radicles, and can therefore be prepared by method No. 1. No compound of these bodies with negative elements has yet been produced. They are in the condition of chemical saturation. Further details of their properties are wanting.

*Aluminium series.*—The only known organo-compounds of this series are aluminic methide, $Al'''(CH^3)^3$, and aluminic ethide, $All'''(C^2H^5)^3$. They are prepared by heating mercuric methide or ethide with excess of aluminium clippings in sealed tubes: *e.g.*

$$3Hg''(CH^3)^2 + Al^2 = 2Al'''(CH^3)^3 + Hg^3.$$

They are spontaneously, inflammable liquids, which decompose water with explosive violence, and react with iodine to form iodo-derivatives and iodide of methyl or ethyl. By regulated exposure to dry air they take up oxygen, forming bodies apparently analogous to boric dioxy-methide and dioxethide (Buckton and Odling). A compound of aluminic ethide with iodide of ethyl had previously been obtained by Cahours § by heating aluminium with iodide of ethyl (ii. 535). *Glucinum* appears to act with iodide of ethyl in a similar manner.

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* Wanklyn, Chem Soc Qu. J. xi. 103.

† Frankland, Proc Roy. Soc. ix. 345.

‡ Cahours, Ann. Ch. Phys. lviii. 17.

§ *Ibid.* [3] lviii. 20.—Buckton and Odling (Proc. Roy. Soc xiv. 19).

**Zinc Series.***—Three bodies belonging to this series are known, viz.:

$$\text{Zinc-methyl, } Zn''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right. \qquad \text{Zinc-ethyl, } Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right. \qquad \text{Zinc-amyl, } Zn''\left\{\begin{matrix}C^5H^{11}\\C^5H^{11}.\end{matrix}\right.$$

They are colourless, transparent, mobile, volatile, and odorous liquids, composed of two gaseous volumes of the hydro-carbon radicle, and one volume of zinc-vapour, the three volumes condensed to two. The methyl- and ethyl-compounds are spontaneously inflammable, burning with a greenish-blue flame: zinc-amyl is spontaneously inflammable in pure oxygen only. All three are saturated compounds, incapable of direct combination. In contact with water, they are instantly decomposed, with formation of hydrated oxide of zinc and hydride of the organic radicle:

$$\underset{\text{Zinc-methyl.}}{Zn''(CH^3)^2} + 2H^2O = Zn''H^2O^2 + \underset{\text{Hydride of methyl.}}{2(CH^3.H).}$$

Gradually treated with dry oxygen so as to avoid too violent action, they pass through two stages of oxidation, illustrated in the case of zinc-ethyl by the following equations:—

$$\underset{\text{Zinc-ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + O = \underset{\text{Ethylate of zinc-ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\OC^2H^5\end{matrix}\right.}$$

$$\underset{\text{Ethylate of zinc-ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\OC^2H^5\end{matrix}\right.} + O = \underset{\text{Ethylate of zinc.}}{Zn''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.}$$

The action of iodine upon organo-zinc compounds differs somewhat from that of oxygen owing to the monatomic character of the negative element. It consists in the successive elimination of the two atoms of hydrocarbon-radicle and their substitution by iodine:

$$\underset{\text{Zinc ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + I^2 = \underset{\text{Iodo-ethide of zinc.}}{Zn''\left\{\begin{matrix}C^2H^5\\I\end{matrix}\right.} + \underset{\text{Iodide of ethyl.}}{C^2H^5I}$$

$$\underset{\text{Iodo-ethide of zinc.}}{Zn''\left\{\begin{matrix}C^2H^5\\I\end{matrix}\right.} + I^2 = \underset{\text{Iodide of zinc.}}{Zn''\left\{\begin{matrix}I\\I\end{matrix}\right.} + \underset{\text{Iodide of ethyl.}}{C^2H^5I.}$$

Organo-zinc compounds behave in a manner exactly analogous in contact with the other halogens.

Reactions like the foregoing point to the applicability of these compounds for effecting the substitution of positive groups for negative elements in compound bodies, an application which has not failed to attract the notice of chemists. In addition to the reactions of this class given above as examples of the formation of organo-metallic bodies by the third method, the following have been realised:

*With Nitric Oxide.*†

$$\underset{\text{Nitric oxide.}}{2N^2O^2} + \underset{\text{Zinc-methyl.}}{Zn''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.} = \underset{\text{Dinitro-methylate of zinc.}}{\left.\begin{matrix}2(N^2CH^3O)\\Zn''\end{matrix}\right\}O^2.}$$

It will be perceived that this reaction is the exact analogue of the one already mentioned in the sodium and potassium series, where carbonic anhydride, treated with sodium-methyl and sodium-ethyl, forms acetic and propionic acids. In fact, dinitro-methylic and dinitro-ethylic acids may be regarded as the analogues of acetic and propionic acids respectively; the nitrogen here sustaining a diatomic character, and replacing an atom of carbon.

*With Sulphurous Oxide.*‡

$$2\overset{iv}{S}O^2 + \underset{\text{Zinc-methyl.}}{Zn''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.} = \underset{\text{Methyl-dithionate of zinc.}}{\left.\begin{matrix}\overset{iv}{S}{}^2(CH^3)^2\overset{''}{O}{}^2\\Zn''\end{matrix}\right\}O^2}$$

$$3\overset{iv}{S}O^2 + \underset{\text{Zinc-ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} = \underset{\text{Ethyl-trithionate of zinc.}}{\left.\begin{matrix}\overset{iv}{S}{}^3(C^2H^5)^2\overset{''}{O}{}^4\\Zn''\end{matrix}\right\}O^2.}$$

---

* Frankland, Chem. Soc. Qu. J. ii. 297, and iii. 44; Phil. Trans. cxlii. 431, and cxlv. 259. Wanklyn, Chem. Soc. Qu. J. xiii. 124. Frankland and Duppa, Chem. Soc. Qu. J. [2] vol. ii. 29. Rieth and Beilstein, Ann. Ch. Pharm. cxxiii. 245. Butlerow, Bull. Soc. Chim. Aug. 1864, p. 116.

† Frankland, Phil. Trans. 1857, p. 59.

‡ Hobson, Chem. Soc. Qu. J. x. 455 and 23.

*With Trichloride of Phosphorus.**

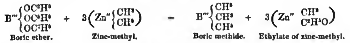
$$2P'''Cl^3 + \underset{\text{Zinc-methyl.}}{3[Zn''(CH^3)^2]} = \underset{\text{Trimethylphosphine.}}{2P'''(CH^3)^3} + 3Zn''Cl^2$$

$$2P'''Cl^3 + \underset{\text{Zinc-ethyl.}}{3[Zn''(C^2H^5)^2]} = \underset{\text{Triethylphosphine.}}{2P'''(C^2H^5)^3} + 3Zn''Cl^2.$$

There is no apparent obstacle to this reaction being pushed to its extreme limit in the case of pentatomic bodies such as phosphorus, arsenic, or antimony. Mr. Buckton has attempted this in the case of antimony; but although evidence of the existence of a pentethide of antimony was obtained, the body could not be isolated nor its composition satisfactorily fixed. The great stability of the triatomic compounds of these bodies will probably present considerable difficulty in the way of obtaining pentatomic compounds of an exclusively positive character, such bodies being doubtless easily resolved into the more stable groupings represented in the following equation:

$$\underset{\text{Antimonic ethide.}}{Sb^v(C^2H^5)^5} = \underset{\text{Triethylstibine.}}{Sb'''(C^2H^5)^3} + \underset{\text{Ethyl.}}{C^2H^5.C^2H^5}$$

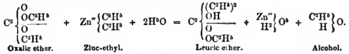
*With Boric Ether.†*



$$\underset{\text{Boric ether.}}{B'''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OC^2H^5\end{matrix}\right.} + \underset{\text{Zinc-methyl.}}{3\left(Zn''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.\right)} = \underset{\text{Boric methide.}}{B'''\left\{\begin{matrix}CH^3\\CH^3\\CH^3\end{matrix}\right.} + \underset{\text{Ethylate of zinc-methyl.}}{3\left(Zn''\begin{matrix}CH^3\\C^2H^5O\end{matrix}\right)}$$

*With Oxalic Ether.‡*

When oxalic ether is heated with zinc-ethyl and water is afterwards added, leucic ether is produced according to the following equation:



$$\underset{\text{Oxalic ether.}}{C^2\left\{\begin{matrix}O\\\underline{OC^2H^5}\\O\\C^2H^5\end{matrix}\right.} + \underset{\text{Zinc-ethyl.}}{Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} + 2H^2O = \underset{\text{Leucic ether.}}{C^2\left\{\begin{matrix}(C^2H^5)^2\\\underline{OH}\\O\\OC^2H^5\end{matrix}\right.} + \left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2 + \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O.}$$

*With Tetrachloride of Silicon.*

$$Si^{iv}Cl^4 + \underset{\text{Zinc-ethyl.}}{2[Zn''(C^2H^5)^2]} = \underset{\text{Silicium-ethyl.}}{Si^{iv}(C^2H^5)^4} + 2Zn''Cl^2.$$

Whilst, on the one hand, organo-zinc-compounds are thus capable of effecting the substitution of their positive organic groups for negative elements, they can, on the other hand, in certain cases replace hydrogen by zinc, forming, for instance, with ammonia and its homologues, a series of zinc-amides. In this direction the following reactions amongst others have been recorded: §

$$\underset{\text{Zinc-ethyl.}}{Zn''(C^2H^5)^2} + \underset{\text{Ammonia.}}{2N'''H^3} = \underset{\text{Zincamide.}}{\overset{''}{N}^2Zn''H^4} + \underset{\text{Hydride of ethyl.}}{2(C^2H^5.H)}$$

$$\underset{\text{Zinc-ethyl.}}{Zn''(C^2H^5)^2} + \underset{\text{Aniline.}}{2[N'''(C^6H^5)H^2]} = \underset{\text{Zincphenylimide.}}{\overset{'''}{N}^2(C^6H^5)^2Zn''H^2} + \underset{\text{Hydride of ethyl.}}{2(C^2H^5.H)}$$

$$\underset{\text{Zinc-ethyl.}}{Zn(C^2H^5)^2} + \underset{\text{Oxamide.}}{\overset{'''}{N}^2(C^2\overset{''}{O}^2)H^4} = \underset{\text{Zincoximide.}}{\overset{'''}{N}^2(C^2O^2)''Zn''H} + \underset{\text{Hydride of ethyl.}}{2(C^2H^5.H)}$$

By losing one atom of alcohol-radicle the organo-zinc-compounds become monatomic compound-radicles, forming compounds which have been but little examined. The following however have been described: ‖

Dinitromethylate of zinc-methyl . . . . $\left.\begin{matrix}N^2CH^3O\\ZnCH^3\end{matrix}\right\}O.$

Dinitroethylate of zinc-ethyl . . . . $\left.\begin{matrix}N^2C^2H^5O\\ZnC^2H^5\end{matrix}\right\}O.$

CADMIUM SERIES.¶—Only one member of this series is known, and that very imperfectly. Its properties appear however to be analogous to those of the zinc-compounds.

TIN SERIES.**—A large number of organo-metallic bodies containing tin have been described. The following will suffice as examples of the several classes of these compounds:

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* Hofmann and Cahours, Phil. Trans. 1857, p. 578.

† Frankland, Phil. Trans. 1862, p. 167.

‡ Frankland, Proc. Roy. Soc. xii. p. 396.

§ Frankland, Proc. Roy. Soc. viii. p. 502.

‖ Frankland, Phil. Trans. 1857, p. 59.

¶ Wanklyn, Chem. Soc. Qu. J. ix. 193.

** Frankland, Phil. Trans. 1852, p. 417, and 1859, p. 401. Cahours and Riche, Compt. rend. xxxv. 91, and xxxvi. 1001. Löwig, Ann. Ch. Pharm. lxxxiv. 308. A. Grimm, Ann. Ch. Pharm. xcii. 383. Buckton, Phil. Trans. for 1859, p. 432. Cahours, Ann. Ch. Phys. lviii. 22. Strecke, Ann. Ch. Pharm. cxxiii. 365.

### *a. Stannous Compounds.*

| | |
|---|---|
| Stannous methide, or Stanmethyl . . | $Sn''(CH^3)^2$. |

### *b. Triatomic Compounds.*

| | |
|---|---|
| Trimethide of tin . . | $[Sn'''(CH^3)^3]^2$ |
| Iodo-dimethide of tin . | $[Sn'''(CH^3)^2I]$. |

### *c. Stannic Compounds.*

| | |
|---|---|
| Stannic methide . . . . . | $Sn^{iv}(CH^3)^4$ |
| Stannic iodo-trimethide . . . . | $Sn^{iv}(CH^3)^3I$ |
| Stannic iodo-dimethide . . . . | $Sn^{iv}(CH^2)^2I^2$. |

It is scarcely necessary to observe that the iodine in the above compounds admits of replacement by any salt-forming radicles and also by oxygen or sulphur.

*Stannous compounds* are oily liquids soluble in alcohol and ether, but insoluble in water, and possess a pungent odour. They cannot be distilled without decomposition, being resolved into stannic compounds and metallic tin. They are in a state of partial chemical saturation only, and therefore perform the part of radicles, combining directly with chlorine, oxygen, &c., and forming well-marked bodies of great stability.

Stannous compounds are diatomic, and unite directly with free oxygen, chlorine, &c., to produce bodies of the stannic form. Thus stannous ethide forms with oxygen, stannic oxidiethide:

$$\underset{\text{Stannous ethide.}}{Sn''(C^2H^5)^2} + O = \underset{\text{Stannic oxidiethide.}}{Sn^{iv}(C^2H^5)^2O''}$$

Stannous compounds have never yet been observed to play a monatomic part. No triatomic compound has been directly formed from a stannous body; the latter, under the influence of iodine, oxygen, &c., seems to pass at once into the stannic form.

*Triatomic compounds* of the form $(Sn'''R^3+)^2$ have hitherto been very little examined. They are oily liquids, uniting directly with negative radicles, forming an extensive series of compounds belonging to the stannic class, a considerable number of which have been studied. The following examples will serve to show the mode in which triatomic compounds of this form pass into bodies of the stannic class:

$$\underset{\text{Tri-ethide of tin.}}{[Sn'''(C^2H^5)^3]^2} + I^2 = \underset{\text{Stannic iodotriethide.}}{2Sn^{iv}(C^2H^5)^3I}.$$

$$\underset{\substack{\text{Stannic iodotri-}\\\text{ethide.}}}{Sn^{iv}(C^2H^5)^3I} + I^2 = \underset{\substack{\text{Stannic}\\\text{ethide.}}}{Sn^{iv}(C^2H^5)^2I^2} + \underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{C^2H^5I}.$$

No reduction of a triatomic compound to a stannous compound has yet been effected, although it can scarcely be doubted that an aqueous solution of diethiodide of tin, for instance, if treated with zinc, would yield stannous ethide. On the other hand, stannic ethide or methide in contact with iodine is transformed into a triatomic compound, viz., diethiodide of tin:

$$\underset{\text{Stannic ethylo-dimethide.}}{2Sn^{iv}(C^2H^5)^2(CH^3)^2} + I^6 = \underset{\substack{\text{Dimethiodide}\\\text{of tin.}}}{2Sn^{iv}(C^2H^5)^2I} + \underset{\substack{\text{Iodide of}\\\text{methyl.}}}{4CH^3I}.$$

Triatomic compounds of the form $\left(Sn'''\begin{cases}R+\\R+\\R-\end{cases}\right)^2$ are very little known. In fact the diethiodide of tin, the production of which from stannic ethylodimethide has just been mentioned, is the only one known with certainty. It is a colourless mobile liquid, boiling with partial decomposition at 208°, and possessing a most insupportable odour, resembling essential oil of mustard. Heated with excess of iodine, it is transformed into stannic iododiethide:

$$\underset{\text{Diethiodide of tin.}}{[Sn'''(C^2H^5)^2I]^2} + I^2 = \underset{\text{Stannic iododiethide.}}{2Sn^{iv}(C^2H^5)^7I^2}.$$

*Stannic compounds* of the form $Sn^{iv}R^4+$ are colourless mobile liquids, possessing a slight ethereal odour. They are volatile without decomposition, and are very stable. Being in the condition of chemical saturation, they are incapable of direct combination. No body can act upon them without expelling one or more atoms of positive radicle. Thus, when heated with hydrochloric acid, stannic ethide yields stannic chlorotriethide and hydride of ethyl:

$$\underset{\text{Stannic ethide.}}{Sn^{iv}(C^2H^2)^4} + HCl = \underset{\substack{\text{Stannic chlorotri-}\\\text{ethide.}}}{Sn^{iv}(C^2H^5)^3Cl} + \underset{\substack{\text{Hydride}\\\text{of ethyl.}}}{C^2H^5.H}.$$

Stannic compounds of the form $\mathrm{Sn^{iv}}\left\{\begin{matrix}\mathrm{R^2}+\\ \mathrm{R}\;-\end{matrix}\right.$ commonly called compounds of sesquistannethyl, have been comparatively well studied. The oxides are, in the anhydrous condition, volatile, limpid, oily liquids which readily unite with water, forming crystalline hydrates which have a powerful alkaline reaction, and neutralise the strongest acids, forming an extensive series of salts. These salts are almost all soluble in water, readily crystallisable, and of a very pungent odour.

Stannic compounds of the form $\mathrm{Sn^{iv}}\left\{\begin{matrix}\mathrm{R^2}+\\ \mathrm{R^2}-\end{matrix}\right.$ have also been very completely investigated. The oxides are white amorphous powders, insoluble in water, alcohol, and ether. They dissolve in hydrochloric, hydriodic, and hydrobromic acids, forming colourless and inodorous salts, which crystallise in fine prisms. Most of the oxysalts can also be obtained in the crystalline form, either from aqueous or alcoholic solutions.

Stannic compounds of this form are readily reduced to stannous compounds; thus, when a piece of zinc is plunged into a solution of stannic chlorodiethide, stannous ethide is produced:

$$\underset{\text{Stannic chlorodiethide.}}{\mathrm{Sn^{iv}(C^2H^5)^2Cl^2}} + \mathrm{Zn''} = \underset{\text{Stannous ethide.}}{\mathrm{Sn''(C^2H^5)^2}} + \mathrm{Zn''Cl^2}.$$

Bismuth Series.*—These bodies have as yet been but very imperfectly investigated. Bismuthous triethide is a colourless or slightly yellow mobile liquid, having an unpleasant odour like that of stibethine. Exposed to the air, it gives off dense yellow fumes, inflames spontaneously, and finally explodes. It is very unstable, begins to decompose at 50° or 60° C., and explodes violently when heated to 150° C., a temperature still below its boiling point. No direct compound of this body has yet been obtained: it behaves like a chemically saturated substance, and when slowly oxidised in contact with water, yields alcohol and hydrated oxide of bismuth.

When an alcoholic solution of mercuric chloride is added to an alcoholic solution of bismuthous ethide, mercuric ethochloride crystallises out, whilst bismuthous dichlorethide remains in solution:

$$\underset{\text{Bismuthous ethide.}}{\mathrm{Bi'''(C^2H^5)^3}} + \mathrm{2Hg''Cl^2} = \underset{\text{Bismuthous dichlorethide.}}{\mathrm{Bi'''(C^2H^5)Cl^2}} + \underset{\text{Mercuric chlorethide.}}{\mathrm{2Hg''(C^2H^5)Cl}}.$$

From the bismuthous dichlorethide, the diiodide and dioxyethide are prepared by double decomposition, whilst the simultaneous action of sulphuretted hydrogen, water, bismuthous ethide, and atmospheric oxygen is said to produce the double compound of bismuthous sulphide and bismuthic sulphotriethide.

Lead Series.†—Plumbic ethide, $\mathrm{Pb^{iv}(C^2H^5)^4}$, and its derivatives only are known in this series.

Plumbic ethide is a colourless limpid fluid, soluble in ether, but insoluble in water, and possessing a faint odour. It is not acted upon by oxygen at ordinary temperatures, but chlorine, bromine, and iodine act violently upon it. Plumbic ethide belongs to the class of saturated bodies, and is consequently incapable of forming compounds. When it is treated with hydrochloric acid, hydride of ethyl separates and plumbic chlorotriethide is formed:

$$\underset{\text{Plumbic ethide.}}{\mathrm{Pb^{iv}(C^2H^5)^4}} + \mathrm{HCl} = \underset{\text{Plumbic chlorotriethide.}}{\mathrm{Pb^{iv}(C^2H^5)^3Cl}} + \underset{\text{Hydride of ethyl.}}{\mathrm{C^2H^5H}}.$$

From plumbic chloro-triethide the sulphate and other salts can be prepared by double decomposition. These salts may also be obtained still more readily from the oxide, which is a crystalline, volatile, pungent body, possessing a powerful alkaline reaction, and attracting carbonic acid from the air.

Mercuric Series.‡—This series is confined to bodies of the mercuric type, no organo-mercurous compound having been yet produced. The following are examples of bodies belonging to this series:

| | |
|---|---|
| Mercuric methiodide . . . . . | $\mathrm{Hg''}\left\{\begin{matrix}\mathrm{CH^3}\\ \mathrm{I}\end{matrix}\right.$ |
| Mercuric ethonitrate . . . . . | $\mathrm{Hg''}\left\{\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{NO^3}\end{matrix}\right.$ |
| Mercuric amylide . . . . . | $\mathrm{Hg''}\left\{\begin{matrix}\mathrm{C^5H^{11}}\\ \mathrm{C^5H^{11}}.\end{matrix}\right.$ |

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* Braad, Ann. Ch. Pharm. lxxxii. 106; Dünhaupt, Ann. Ch. Pharm. xcii. 371.

† Löwig, Ann. Ch. Pharm. lxxxviii. 318; Buckton, Phil. Trans. 1859, p. 417.

‡ Frankland, Phil. Trans. 1852, p. 4.6, and Phil. Trans. 1859, p. 409; Dünhaupt, Ann. Ch. Pharm. xcii. 371; Strecker, Ann. Ch. Pharm. xcii. 57; Buckton, Phil. Trans. 1858, p. 163, and 1859, p. 417. Frankland and Duppa, Journ. of Chem. Soc. xvi. p. 415.

Mercuric methide, mercuric ethide and mercuric amylide are colourless, ethereal, volatile liquids, insoluble in water, but soluble in alcohol and ether, and possessing great stability. They are in a state of maximum saturation, and cannot therefore unite with any other body without the displacement of an equivalent of positive radicle. Thus with bromine, mercuric ethide gives bromide of ethyl and mercuric ethylobromide:

$$\underset{\text{Mercuric ethide.}}{Hg''(C^2H^5)^2} + Br^2 = \underset{\text{Mercuric ethylobromide.}}{Hg''(C^2H^5)Br} + \underset{\text{Bromide of ethyl.}}{C^2H^5Br.}$$

Mercuric methide possesses the highest specific gravity of any known non-metallic liquid (3·069). Flint-glass consequently floats upon its surface. Brought into contact with mercuric iodide, mercuric methide, mercuric ethide and mercuric amylide are converted respectively into mercuric methiodide, mercuric ethiodide and mercuric amyliodide:

$$\underset{\text{Mercuric methide.}}{Hg''(CH^3)^2} + Hg''I^2 = \underset{\text{Mercuric methiodide.}}{2[Hg''(CH^3)I].}$$

The reaction with mercuric chloride is exactly analogous. The hydrates of mercuric methoxide and mercuric ethoxide are caustic alkaline bases, capable of expelling ammonia from its salts, and behaving in a manner similar to the corresponding monatomic compounds of tin and lead. The remaining mercury-compounds, which may be considered as derivatives of these two bodies, are represented in the above list by the iodides and nitrates: they generally crystallise very readily, and, with the exception of the haloid compounds, are soluble in water. The behaviour of mercuric methide, ethide and amylide in contact with zinc has already been described as the basis of a method for procuring the zinc-compounds of the respective hydrocarbon radicles. When the iodide, bromide, or chloride of an organo-mercurial body is treated with an organo-zinc compound, the negative element becomes replaced by the alcohol-radicle of the zinc-compound; thus, when mercuric methiodide is treated with zinc-methyl, mercuric methide is produced. And it is believed that by acting upon mercuric ethochloride with zinc-methyl, mercuric ethylomethide is formed:

$$\underset{\text{Mercuric ethochloride.}}{2[Hg''(C^2H^5)Cl]} + \underset{\text{Zinc-methyl.}}{Zn''(CH^3)^2} = \underset{\text{Mercuric ethylomethide.}}{2[Hg''(C^2H^5)(CH^3)]} + Zn''Cl^2,$$

but this body has not yet been obtained in a state of purity; distillation gradually resolves it into mercuric methide and mercuric ethide:

$$\underset{\text{Mercuric ethylomethide.}}{2[Hg''(C^2H^5)(CH^3)]} = \underset{\text{Mercuric methide.}}{Hg''(CH^3)^2} + \underset{\text{Mercuric ethide.}}{Hg''(C^2H^5)^2.}$$

ANTIMONY SERIES.[*]—This important series of organo-metallic bodies contains a greater number and variety of compounds than any other, with the exception of the arsenic series. The remarkable polyatomic character of antimony and arsenic not only renders the possible number of their organo-compounds very large, but the variations in the proportions of the positive and negative molecules gives an extremely wide range to their chemical character, extending, as it does, from highly caustic bases on the one hand to powerful bibasic acids on the other. The following are the principal compounds belonging to this series:

| | |
|---|---|
| Trimethylstibine | $Sb'''(CH^3)^3$. |
| Antimonic Trimethoxide | $Sb^{v}(CH^3)^3O$. |
| Iodide of tetramethylstibonium or antimonic tetramethiodide | $Sb^{v}(CH^3)^4I$. |
| Hydrate of tetramethylstibonium or antimonic tetramethylhydrate | $Sb^{v}(CH^3)^4(HO)$. |
| Antimonic Trimethosulphate | $Sb^{v}(CH^3)^3(SO^4)''$. |
| Antimonic Triamylnitrate | $Sb^{v}(CH^3)^3(NO^3)^2$. |

It is remarkable that we have as yet no decisive evidence in this series, of the existence of a compound corresponding to cacodyl. It is true that such a body has been described under the name of *stibbiamyl*, but subsequent experiments have failed to confirm its existence. Amongst organo-antimony compounds, therefore, the most simple form is $Sb'''R^3+$. Bodies of this form are the analogues of ammonia, and need not be here further noticed. The pentatomic organo-antimonial compounds of the form $Sb^{v}\begin{cases}R^4+\\R-\end{cases}$ are also the true analogues of ammonium-compounds.

The remaining compounds of this series are constructed upon the model $Sb^{v}\begin{cases}R^3+\\R^2-.\end{cases}$ When two atoms of $R-$ are replaced by diatomic oxygen, these compounds constitute what may be termed biacid antimony bases. They are formed either by the direct union of the stibamines $\mathrm{Sb'''R^3}+$ with oxygen:

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[*] Löwig, Ann. Ch. Pharm. lxxv. 315, 327; Landolt, *ibid.* lxxviii. 91; Buckton, Chem. Soc. Qu. J. xiii. 115; Hofmann, *ibid.* xi. 316.

$$\mathrm{Sb'''}\left\{\begin{matrix}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\end{matrix}\right. \quad + \quad \mathrm{O} \quad = \quad \mathrm{Sb^v}\left\{\begin{matrix}\mathrm{R^3}+\\ \mathrm{O''}\end{matrix}\right.$$

or as hydrates by the decomposition of the corresponding haloïd compounds by means of potash: thus—

$$\mathrm{Sb^v}\left\{\begin{matrix}\mathrm{R^3}+\\ \mathrm{Cl^2}\end{matrix}\right. \quad + \quad \mathrm{2KHO} \quad = \quad \mathrm{Sb^v}\left\{\begin{matrix}\mathrm{R^3}+\\ \mathrm{(OH)^2}\end{matrix}\right. \quad + \quad \mathrm{2KCl.}$$

The stibamines, although in other respects the perfect analogues of the nitramines, here evidently exhibit a much more highly positive character, uniting with oxygen so energetically as to be spontaneously inflammable in the lower portion of the series.

The biacid antimony bases are colourless, transparent, amorphous, and viscous bodies; the ethyl base is easily soluble in water and alcohol, but somewhat less soluble in ether. They possess a bitter taste, are non-volatile, and do not suffer any change when exposed to the air. Treated with potassium they are reduced to stibamines:

$$\mathrm{Sb}\left\{\begin{matrix}\mathrm{R^3}+\\ \mathrm{(OH)^2}\end{matrix}\right. \quad + \quad \mathrm{2K} \quad = \quad \mathrm{Sb'''}\left\{\begin{matrix}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\end{matrix}\right. \quad + \quad \mathrm{2KHO.}$$

Fuming nitric acid decomposes the biacid bases with ignition; but when they are treated with dilute nitric or other acid, the respective biacid salts are produced. The oxysalts are soluble in water or alcohol; most of them crystallise without much difficulty, as do also the antimonic biniodides; but antimonic triethobromide and triethochloride are liquids not volatile without decomposition, insoluble in water, but soluble in alcohol and ether.

The existence of antimonic triethoxiodide has been proved by Strecker. It had previously been regarded by Merck as a protoiodide of stibethine ($\mathrm{Sb(C^4H^5)^3I}$).

ARSENIC SERIES.*—This series is perhaps the most important and interesting amongst organo-metallic bodies; it contains the first discovered organo-metal, cacodyl, the classical investigation of which by Bunsen not only imparts a completeness to our knowledge of this series, but has afforded the clue to the successful interpretation of many phenomena met with in other analogous families. It will be convenient to divide its very numerous members into three groups.

A. Organo-arsenical compounds of the type $\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}\mathrm{R^3}\\ \mathrm{R^3}\end{matrix}\right.$

B. Organo-arsenical compounds of the type $\mathrm{As'''R^3}$.

C. Organo-arsenical compounds of the type $\mathrm{As^vR^5}$.

All arsenical compounds permit of being arranged under these three types. The following are a few of the principal bodies already investigated:

A. Organo-arsenical compounds of the Type $\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}\mathrm{R^3}\\ \mathrm{R^3}\end{matrix}\right.$

| | |
|---|---|
| Cacodyl | $\mathrm{As^2(CH^3)^4}$ |
| Ethylic cacodyl | $\mathrm{As^2(C^2H^5)^4}$. |

B. Organo-arsenical compounds of the Type $\mathrm{As'''R^3}$.

| | |
|---|---|
| Chloride of cacodyl | $\mathrm{As'''(CH^3)^2Cl}$ |
| Chloride of cacoplatyl | $\mathrm{As'''(CH^3)(CPt'''H)Cl}$ |
| Arsenious oxymethide | $\mathrm{As'''(CH^3)O''}$ |
| Arsenious dichloromethide | $\mathrm{As'''(CH^3)Cl^2}$ |
| Trimethylarsine | $\mathrm{As'''(CH^3)^3}$. |

C. Organo-arsenical compounds of the Type $\mathrm{As^vR^5}$.

This group may be conveniently divided into four families or sub-types, viz.:

*a.* Bodies of the form $\mathrm{As^v}\left\{\begin{matrix}\mathrm{R}\ +\\ \mathrm{R^4}-\end{matrix}\right.$ and their derivatives:

| | |
|---|---|
| Monomethyl-arsenic acid | $\mathrm{As^v(CH^3)O''(HO)^2}$ |
| Arsenic oxydichlormethide | $\mathrm{As^v(CH^3)O''Cl^2}$ |
| Arsenic tetrachlormethide | $\mathrm{As^v(CH^3)Cl^4}$. |

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* Cadet (1760), Mém. de Math. et Phys. de Savants étrang. iii. 633; Thénard, Ann. Ch. lii. 54. Bunsen, Ann. Ch. Pharm. xxiv. 27; xxvii. 1; xiii. 14; xlvi. 1. Frankland, Ch. Soc. Qu. J. ii. 299; Cahours et Riche, Compt. rend. xxxvi. 1001; Landolt, Ann. Ch. Pharm. lxxxix. 301; Hofmann, Chem. Soc. Qu. J. xi. 316. Baeyr, Ann. Ch Pharm. cvii. 257; cv. 265.

*b.* Bodies of the form $\mathrm{As}^{v}\left\{\begin{matrix}R^2+\\R^3-\end{matrix}\right.$, and their derivatives:

| | |
|---|---|
| Cacodylic acid . . . . . . | $\mathrm{As}^{v}(CH^3)^2O''(HO)$ |
| Terchloride of cacodyl . . . . | $\mathrm{As}^{v}(CH^3)^2Cl^3$. |

*c.* Bodies of the form $\mathrm{As}^{v}\left\{\begin{matrix}R^3+\\R-\end{matrix}\right.$, and their derivatives:

| | |
|---|---|
| Arsenic triethoxide . . . . . | $\mathrm{As}^{v}(C^2H^5)^3O''$ |
| Arsenic triethosulphate . . . . | $\mathrm{As}^{v}(C^2H^5)^3(SO^4)''$ |
| Arsenic triethochloride . . . . | $\mathrm{As}^{v}(C^2H^5)^3Cl^2$. |

*d.* Bodies of the form $\mathrm{As}^{v}\left\{\begin{matrix}R^4+\\R-\end{matrix}\right.$

| | |
|---|---|
| Hydrated oxide of tetramethylarsonium or arsenic tetramethydrate . . . . . . . . | $\mathrm{As}^{v}(CH^3)^4(HO)$ |
| Iodide of tetramethylarsonium or arsenic tetramethiodide . . . . . . . . . . | $\mathrm{As}^{v}(CH^3)^4I$. |
| Nitrate of dimethyl-diethylarsonium or arsenic dimethyl-diethylnitrate . . . . . . | $\mathrm{As}^{v}(CH^3)^2(C^2H^5)^2(NO^3)$. |

The organo-arsenical compounds belonging to the type $\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}R^2\\R^2\end{matrix}\right.$ contain only positive radicles. They are volatile poisonous liquids, insoluble in water, but very soluble in alcohol and ether, and possess an insupportable odour. The lower members of the family are spontaneously inflammable, whilst the higher ones also rapidly oxidise in air. They unite with negative elements with great energy, manifesting in their combinations either a monatomic or a triatomic character, and producing bodies either of the form $\mathrm{As}'''\left\{\begin{matrix}R^2+\\R-\end{matrix}\right.$ or $\mathrm{As}^{v}\left\{\begin{matrix}R^2+\\R^3-\end{matrix}\right.$. Thus cacodyl forms with chlorine, chloride of cacodyl and trichloride of cacodyl:

$$\underset{\text{Cacodyl.}}{\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}(CH^3)^2\\(CH^3)^2\end{matrix}\right.} \quad + \quad Cl^2 \quad = \quad \underset{\text{Chloride of cacodyl.}}{2[\mathrm{As}'''(CH^3)^2Cl]}.$$

$$\underset{\text{Cacodyl.}}{\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}(CH^3)^2\\(CH^3)^2\end{matrix}\right.} \quad + \quad Cl^6 \quad = \quad \underset{\text{Trichloride of cacodyl.}}{2[\mathrm{As}^{v}(CH^3)^2Cl^3]}.$$

Heated to 400°, cacodyl splits up into metallic arsenic, hydride of methyl, and olefiant gas:

$$\underset{\text{Cacodyl.}}{\overset{'''}{\mathrm{As}}{}^2(CH^3)^4} \quad = \quad As^2 \quad + \quad \underset{\text{Hydride of methyl.}}{2(CH^3.H)} \quad + \quad \underset{\text{Ethylene.}}{C^2H^4}.$$

Bodies of this type can be regenerated by reducing agents from many of their monatomic compounds; thus chloride of cacodyl and metallic zinc give cacodyl and chloride of zinc:

$$2\mathrm{As}'''\left\{\begin{matrix}(CH^3)^2\\Cl\end{matrix}\right. \quad + \quad Zn \quad = \quad \mathrm{As}^2\left\{\begin{matrix}(CH^3)^2\\(CH^3)^2\end{matrix}\right. \quad + \quad Zn''Cl^2.$$

Organo-arsenical compounds of the type $\mathrm{As}'''R^3$ are of three forms, viz.:

$$(1)\quad \mathrm{As}'''R^3+ \qquad (2)\quad \mathrm{As}'''\left\{\begin{matrix}R^2+\\R-\end{matrix}\right. \qquad (3)\quad \mathrm{As}'''\left\{\begin{matrix}R+\\R^2-\end{matrix}\right.$$

Those belonging to the first are termed *arsines*, and are the analogues of ammonia; but, like the corresponding antimony compounds, in addition to their alkaloïd function, they have the power of combining with two negative atoms, forming bodies of the sub-type $\mathrm{As}^{v}\left\{\begin{matrix}R^3+\\R^2-\end{matrix}\right.$. Thus triethylarsine combines with oxygen to form arsenic oxytriethide. The lower members of the type possess this property to such an extent as to render them spontaneously inflammable in the air.

Compounds belonging to the second of the above forms are produced by the direct combination of the cacodyls with negative elements. When the negative element is oxygen, the diatomic character of the latter doubles the type, which then becomes $\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}R^2+\\R^2+\\O''\end{matrix}\right.$. The oxides are bases of comparatively feeble power, slowly combining with water and two additional atoms of oxygen, to form acids. Thus oxide of cacodyl, by exposure to air and moisture, slowly passes into cacodylic acid:

$$\underset{\text{Oxide of cacodyl.}}{\overset{'''}{\mathrm{As}}{}^2(CH^3)^4O''} \quad + \quad \overset{''}{O}{}^2 \quad + \quad H^2O \quad = \quad \underset{\text{Cacodylic acid.}}{2\mathrm{As}^{v}(CH^3)^2O''(OH)}.$$

The chlorine, bromine, and iodine compounds of the form we are now considering are volatile neutral bodies, which may be regarded as the haloïd salts of cacodyl Heated in contact with platinic chloride, the cacodyl presents an interesting reaction two atoms of hydrogen in the chloride of cacodyl become replaced by a diatonic molecule of platinum, producing chloride of cacoplatyl.

$$\underset{\text{Chloride of cacodyl.}}{\mathrm{As'''}\left\{\begin{matrix}\mathrm{CH^3}\\\mathrm{CH^3}\\\mathrm{Cl}\end{matrix}\right.} + \mathrm{Pt''Cl^2} = \underset{\text{Chloride of cacoplatyl.}}{\mathrm{As'''}\left\{\begin{matrix}\mathrm{CH^3}\\\mathrm{CPt''H}\\\mathrm{Cl}\end{matrix}\right.} + \mathrm{2HCl.}$$

Cacoplatyl forms a series of compounds analogous to those of cacodyl.

The only compounds of the third form yet known belong to the methylic group. Arsenious oxymethide is a crystalline body of a neutral character, soluble in water, alcohol and ether, unchanged by exposure to air, but transformed by distillation with hydrate of potassium into arsenious acid and oxide of cacodyl:

$$\underset{\text{Arsenious oxymethide.}}{4\mathrm{As'''}\left\{\begin{matrix}\mathrm{CH^3}\\\mathrm{O''}\end{matrix}\right.} + 2\left.\begin{matrix}\mathrm{K}\\\mathrm{H}\end{matrix}\right\}\mathrm{O''} = \overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}\overset{''}{\mathrm{O}}{}^2\\\mathrm{OK}\\\mathrm{OK}\end{matrix}\right. + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O''} + \underset{\text{Oxide of cacodyl.}}{\overset{'''}{\mathrm{As}}{}^2\left\{\begin{matrix}\mathrm{(CH^3)^2}\\\mathrm{(CH^3)^2}\\\mathrm{O''}\end{matrix}\right.}$$

Hydrochloric acid converts it into arsenious dichlormethide:—

$$\underset{\text{Arsenious oxymethide.}}{\mathrm{As'''}\left\{\begin{matrix}\mathrm{CH^3}\\\mathrm{O''}\end{matrix}\right.} + \mathrm{2HCl} = \underset{\text{Arsenious dichlormethide.}}{\mathrm{As'''}\left\{\begin{matrix}\mathrm{CH^3}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right.} + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O''}.$$

Hydrobromic and hydriodic acids produce a perfectly analogous change, whilst sulphuretted hydrogen transforms it into arsenious sulphomethide.

The chlorine, bromine, and iodine compounds are neutral bodies of considerable stability; the two former are liquid, the latter solid and crystalline. By the action of chlorine or oxidising agents, they are transformed into bodies of the form $\mathrm{As^v}\left\{\begin{matrix}\mathrm{R}\,+\\\mathrm{R^4}\,-\end{matrix}\right.$

Organo-arsenical compounds have been more thoroughly investigated in the direction of the type $\mathrm{As^vR^5}$ than in any other; consequently we find these bodies rather numerously represented, especially under the subtype $\mathrm{As^v}\left\{\begin{matrix}\mathrm{R^4}\,+\\\mathrm{R}\,-\end{matrix}\right.$ which latter bodies are the strict analogues of the compounds of ammonium.

The *Sub-type* $\mathrm{As^v}\left\{\begin{matrix}\mathrm{R}\,+\\\mathrm{R^4}\,-\end{matrix}\right.$ has yet only been explored in the methylic group. The oxygen compound constitutes anhydrous monomethyl-arsenic acid, a direct derivative from arsenious oxymethide:

$$\underset{\text{Arsenious oxymethide.}}{\mathrm{As'''(CH^3)O''}} + \mathrm{Ag^2O''} = \underset{\text{Monomethylarsenic acid.}}{\mathrm{As^v(CH^3)}\overset{''}{\mathrm{O}}{}^2} + \mathrm{2Ag.}$$

This acid is dibasic, forming stable and well-defined crystallisable salts, the formulæ of which are represented by the general expression: $\mathrm{As^v(CH^3)O''(MO)^2}$.

The chlorine compound is exceedingly unstable; it may however be formed at −19° C., but is transformed at 0° C. into arsenious chloride and chloride of methyl:

$$\underset{\text{Arsenic tetrachlormethide.}}{\mathrm{As^v(CH^3)Cl^4}} = \mathrm{As'''Cl^3} + \underset{\text{Chloride of methyl.}}{\mathrm{CH^3Cl.}}$$

Arsenic oxydichlormethide is a somewhat more stable body formed by the direct union of chlorine with arsenious oxymethide.

$$\underset{\text{Arsenious oxymethide.}}{\mathrm{As'''(CH^3)O}} + \mathrm{Cl^2} = \underset{\text{Arsenic oxydichlormethide.}}{\mathrm{As^v(CH^3)O''Cl^2.}}$$

Nevertheless, even this compound readily decomposes, with evolution of chloride of methyl.

*Sub-type* $\mathrm{As^v}\left\{\begin{matrix}\mathrm{R^2}\,+\\\mathrm{R^3}\,-\end{matrix}\right.$ The oxygen-compounds are feeble monobasic acids of which cacodylic acid may be regarded as the representative. They are derived from the bodies $\overset{\mathrm{a}}{\mathrm{As}}{}^2\left\{\begin{matrix}\mathrm{R^2}\,+\\\mathrm{R^2}\,+\\\mathrm{O}\end{matrix}\right.$ by direct oxidation as already described. Cacodylic acid is remarkable for its stability; neither fuming nitric acid nor a mixture of sulphuric and chromic acids attack it, even at the boiling point, and it may be heated to 200° without alteration. Although it is soluble in water and contains upwards of 54 per cent. of arsenic, yet it is not in the least poisonous. Several agents reduce cacodylic acid to the arsenious or even to the diatomic form. Thus phosphorus acid transforms it into cacodyl:

$$\underset{\text{Cacodylic acid.}}{2\mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}\mathrm{CH}^3\\ \mathrm{CH}^3\\ \mathrm{O}''\\ \mathrm{OH}\end{matrix}\right.} + 3\mathrm{P}'''\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. = \underset{\text{Cacodyl.}}{2\mathrm{As}'''\left\{\begin{matrix}\mathrm{CH}^3\\ \mathrm{CH}^3\end{matrix}\right.} + 2\mathrm{H}^2\mathrm{O} + \underset{\text{Phosphoric acid.}}{3\mathrm{P}^{\mathrm{v}}\left\{\begin{matrix}\mathrm{O}''\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.}$$

Zinc also produces the same result. Hydriodic acid gas converts cacodylic acid into arsenious dimethiodide:

$$\mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}(\mathrm{CH}^3)^2\\ \mathrm{O}''\\ \mathrm{OH}\end{matrix}\right. + 3\mathrm{HI} = \mathrm{As}'''\left\{\begin{matrix}(\mathrm{CH}^3)^2\\ \mathrm{I}\end{matrix}\right. + \mathrm{I}^2 + 2\mathrm{H}^2\mathrm{O}.$$

The acid character of this body is so slightly marked as to render it capable of forming compounds in which it appears to play the part of a base. Thus with hydrofluoric, hydrochloric and hydrobromic acids, it forms the following compounds:

$$\mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}(\mathrm{CH}^3)^2\\ (\mathrm{HO})^2,\\ \mathrm{F}\end{matrix}\right. \qquad \mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}(\mathrm{CH}^3)^2\\ (\mathrm{HO})^2\\ \mathrm{Cl}\end{matrix}\right. \quad \text{and} \quad \mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}(\mathrm{CH}^3)^2\\ (\mathrm{HO})^2\\ \mathrm{Br}\end{matrix}\right.$$

Sulphocacodylic acid has not yet been isolated, but its salts present the same relations to those of cacodylic acid, as salts of sulphur-acids generally bear to those of oxy-acids. Their formula is, $\mathrm{As}^{\mathrm{v}}(\mathrm{CH}^3)^2\mathrm{S}''(\mathrm{MS})$.

The *Sub-type* $\mathrm{As}^{\mathrm{v}}\left\{\begin{matrix}\mathrm{R}^3 & +\\ \mathrm{R}^3 & -\end{matrix}\right.$ has hitherto been very little explored, but so far as it is known, its members bear so close a resemblance to their analogues in the antimony-series, as to require no further notice.

TELLURIUM SERIES.*—The close relations of tellurium to sulphur and selenium place the bodies of this series in the same position with regard to the sulphides and selenides of the alcohol-radicles as the antimony and arsenic series stand in relation to the corresponding compounds of phosphorus and nitrogen.

The following are some of the chief bodies belonging to this series:

| | |
|---|---|
| Tellurium-methyl . . . . | $\mathrm{Te}(\mathrm{CH}^3)^4$ |
| Tellurous dimethoxide . . . . | $\mathrm{Te}(\mathrm{CH}^3)^2\mathrm{O}''$ |
| Tellurous diethiodide . . . . | $\mathrm{Te}(\mathrm{C}^2\mathrm{H}^5)^2\mathrm{I}^2$ |
| Tellurous diethosulphate . . . | $\mathrm{Te}(\mathrm{C}^2\mathrm{H}^5)^2(\mathrm{SO}^4)''$. |

The compounds of the alcohol-radicles with tellurium are volatile liquids of most unbearable odour. They oxidise readily in contact with air, forming the respective oxides. Tellurium-amyl has not yet been obtained in a state of purity.

The oxides of these bodies are powerful bases, expelling ammonia from its salts, and attracting carbonic acid from the air. They form salts of considerable stability, which, as well as the oxides themselves, yield the original organo-tellurium compounds when treated with sulphurous acid:

$$\underset{\substack{\text{Tellurous}\\ \text{diethoxide.}}}{2\mathrm{Te}^{\mathrm{iv}}\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^5)^2\\ \mathrm{O}''\end{matrix}\right.} + \underset{\substack{\text{Sulphurous}\\ \text{acid.}}}{2\mathrm{S}^{\mathrm{iv}}\left\{\begin{matrix}\mathrm{O}''\\ (\mathrm{OH})^2\end{matrix}\right.} = \underset{\substack{\text{Tellurium}\\ \text{ethyl.}}}{\overset{\mathrm{v}}{\mathrm{Te}}{}^2\left\{\begin{matrix}(\mathrm{C}^2\mathrm{H}^5)^2\\ (\mathrm{C}^2\mathrm{H}^5)^2\end{matrix}\right.} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2\mathrm{S}^{\mathrm{vi}}\left\{\begin{matrix}\mathrm{O}^2\\ (\mathrm{OH})^2\end{matrix}\right.}$$

### *Constitution of Organo-metallic Bodies.*

Organo-metallic bodies may be regarded as constructed upon the types of the inorganic chlorides, sulphides, oxides, &c., of the respective metals which they contain, the chlorine, oxygen, sulphur, &c., being replaced in equivalent proportion and frequently step by step by the alcohol-radicles.

A reference to the formulæ of organo-potassium, sodium, and lithium compounds when disentangled from that of the zinc-compound with which they have hitherto remained inseparately associated, shows that they are formed upon the monatomic type of the protochlorides, &c., of these metals, MCl.

The zinc, cadmium, and mercury compounds are all formed upon the diatomic type, represented by the chloride of zinc, $\mathrm{Zn}''\mathrm{Cl}^2$

In like manner organo-aluminium compounds are formed upon the type of the trichloride of that metal, $\mathrm{Al}'''\mathrm{Cl}^3$.

Organo-tin compounds are represented by the three chlorides of tin: $\mathrm{Sn}''\mathrm{Cl}^2$, $\mathrm{Sn}'''\mathrm{Cl}^3$, $\mathrm{Sn}^{\mathrm{iv}}\mathrm{Cl}^4$.

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* Wöhler, Ann. Ch. Pharm. xxxv. 112, lxxxiv. 69; Mallet, *ibid.* lxxix. 223; Wöhler and Dean, *ibid.* xciii. 233.

The compounds of the bismuth-series are represented by the trichloride of bismuth and by bismuthic acid: $Bi'''Cl^3$ and $Bi^v\left\{\begin{matrix}O'' \\ (OH)^3\end{matrix}\right.$

Organo-lead compounds are arranged under the type of peroxide of lead: $Pb^{iv}\left\{\begin{matrix}O'' \\ O''\end{matrix}\right.$

The *arsenic* and *antimony* series have for their types the following inorganic compounds:

$$\overset{''}{A}s^2\left\{\begin{matrix}S'' \\ S''\end{matrix}\right. \qquad As'''Cl^3 \qquad As^v\left\{\begin{matrix}\overset{''}{O}{}^2 \\ OH\end{matrix}\right. \qquad Sb'''Cl^3 \qquad Sb^vCl^5.$$

The inorganic models for the tellurium series are chloride of tellurium and tellurous acid: $Te''Cl^2$ and $Te^{iv}O^3$.

Occasionally an abnormal compound has made its appearance, such as ethostibilic acid, $Sb^2(C^2H^5)^2O^5$ or iodide of triethylstibine, $Sb(C^2H^5)^3J$; but further research has invariably demonstrated the incorrectness of such formulæ and the conformity of the bodies with the normal inorganic types. Indeed this law may now be regarded as completely established so as to be applicable to the control of the formulæ of new organo-metallic bodies.

From the point of view thus afforded, it is interesting to watch the effect of the substitution in metallic compounds, of basylous or positive for chlorous or negative radicles. Such a substitution affords striking evidence of the dependence of the chemical character of a compound upon that of each individual constituent. The highly polyatomic metals, such as arsenic and antimony, exhibit this dependence in the most conclusive manner. Thus tribasic arsenic acid, by the substitution of methyl for half an atom of oxygen, yields the dibasic monomethyl-arsenic acid, a well-defined acid of considerable energy, though inferior in chlorous power to arsenic acid. The like substitution of a whole equivalent of oxygen by methyl reduces the chlorous character of the body to the comparatively feeble condition in which we find it in cacodylic acid, which is incapable of forming an ammonia-salt. A similar substitution for the third time, overpowers the acid attribute of the compound altogether, and we now have a feeble biacid base, the arsenic oxytrimethide, which again, by the exchange of oxygen for a fourth atom of methyl, is transformed into the oxide of tetramethylarsonium, a base of such energy as to be comparable with the caustic alkalis themselves.

The behaviour of the organo-metallic bodies teaches a doctrine which affects chemical compounds in general, and which may be called the doctrine of atomic saturation. Each element is capable of combining with a certain limited number of atoms; and this number can never be exceeded, although the energy of its affinities may have been increased by combination up to this point. Thus zinc appears to attain its atomic saturation by uniting with two atoms of another body; in other words it is diatomic; consequently the zinc compounds of the alcohol-radicles, notwithstanding their intense affinities, are incapable of direct union with other bodies. The action of chlorous elements upon them is one of substitution, not of combination. Polyatomic metals exhibit the same phenomenon. An atom of tin cannot combine with more than four atoms, an atom of arsenic or antimony with more than five atoms of other bodies; but in the combination of polyatomic metals, we frequently notice between the lowest and the highest compound one or more intermediate points of exalted stability; thus antimony has a triatomic stage of comparative stability; nitrogen, phosphorus, and arsenic, whilst exhibiting a similar triatomic stage, have also a diatomic one, though of greatly inferior stability; whilst the existence of nitrous oxide and of the organic compounds recently discovered by Griess renders it more than probable that nitrogen has a third and monatomic stage.

In bodies possessing at least one stage of stability below saturation, and in which all the atoms united with the polyatomic element are of the same kind, the stage of maximum stability is very rarely that of saturation. Thus, in nitrogen, arsenic, and bismuth compounds of the kind just mentioned, the stage of maximum stability is decidedly the triatomic one; in antimonial compounds of a similar nature the triatomic is also, though less decidedly, the stage of maximum stability, whilst in phosphorus compounds the points of maximum stability and of saturation generally coincide. When, however, the atoms united with the polyatomic element are not of the same kind, then the stage of maximum stability usually coincides with that of saturation. Thus the oxide or dichloride of triethylarsine or triethylstibine are more stable than triethylarsine, or triethylstibine themselves; but this pentatomic stability reaches its climax in arsonium, stibonium, and phosphonium compounds, as it does also in the corresponding compounds of nitrogen, although the latter element exhibits a much stronger tendency towards universal triatomic stability than its chemical associates.

In polyatomic organo-metallic bodies, it is remarkable that, with few exceptions, the positive hydrocarbons hold their position much more tenaciously than the associated negative constituents; and we thus frequently find the former accompanying the metal through a vast number of compounds. Hence the group formed by the metal and positive hydrocarbons has come to be regarded as a compound radicle. Thus cacodyl is conceived to be the radicle of the whole series of cacodyl compounds. But however great may be the convenience of this mode of viewing organo-metallic compounds, and the same mode has notoriously been extended to nearly all organic bodies, it must not be forgotten that it is a purely artificial distinction, which has no real existence, either in the case of organo-metallic bodies, or in that of organic bodies in general.

A close examination of the habits of the so-called organo-metallic radicles shows clearly, that their atomic power depends upon their position with regard to the stages of stability and maximum saturation; thus they are monatomic when the number of positive groups is one less than that required to reach either the maximum saturation of the metal, or a lower stage of stability. Cacodyl and tetramethylarsonium (the single atom), for instance, are monatomic radicles, because they are respectively one atom short of the stage of stability, and of maximum saturation:

| Monatomic stage. | Stage of stability. |
|---|---|
| $As''' \left\{ \begin{matrix} CH^3 \\ CH^3 \end{matrix} \right.$ | $As''' \left\{ \begin{matrix} CH^3 \\ CH^3 \\ Cl \end{matrix} \right.$ |
| Cacodyl. | Chloride of cacodyl. |
| Monatomic stage. | Stage of maximum saturation. |
| $As^v \left\{ \begin{matrix} CH^3 \\ CH^3 \\ CH^3 \\ CH^3 \end{matrix} \right.$ | $As^v \left\{ \begin{matrix} CH^3 \\ CH^3 \\ CH^3 \\ CH^3 \\ Cl \end{matrix} \right.$ |
| Tetramethyl-arsonium. | Chloride of tetramethylarsonium. |

It is obvious that a compound radicle, the number of whose positive atoms is below that of a stage of stability, can have a double atomic character. Thus cacodyl is sometimes monatomic, as in oxide of cacodyl; and sometimes triatomic, as in cacodylic acid. Again arsenio-monomethyl ($AsCH^3$) is diatomic in arsenious oxymethide, $As''' \left\{ \begin{matrix} CH^3 \\ O'' \end{matrix} \right.$, and tetratomic in monomethylarsenic acid: $As^v \left\{ \begin{matrix} CH^3 \\ O'' \\ (OH)^2 \end{matrix} \right.$ E. F.

**ORGANUM.** See MARJORAM.

**OROPION.** Syn. with ROCK-SOAP.

**ORPIMENT.** Native trisulphide of arsenic (i. 387).

**ORSEILLE.** Syn. with ARCHIL.

**ORSELLESIC ACID.** Syn. with ORSELLINIC ACID.

**ORSELLIC ACID.** Stenhouse designated the acid obtained from South American *Roccella*, by maceration with milk of lime, &c., as α-orsellic, and that prepared in like manner from South African *Roccella* as β-orsellic acid. The former is very much like lecanoric acid (iii. 565), and perhaps identical with it. The latter is contained, together with roccellinin (*q. v.*) in the precipitate thrown down by hydrochloric acid from the lime-extract of the Cape lichen; on exhausting this precipitate repeatedly with water, the roccellinin remains undissolved, while the β-orsellic acid crystallises from the filtrate. It appears to be somewhat less soluble in boiling water than α-orsellic acid, and gives a black precipitate with acetate of lead. It has however the same composition as α-orsellic and lecanoric acid, forms salts exactly resembling the latter, and behaves in the same manner with alcohol, alkalis, hypochlorites, &c. The two acids are therefore often regarded as identical. (See Gm. xii. 377; xvi. 294; Gerh. iii. 797.)

**ORSELLINIC ACID.** $C^8H^8O^4$. *Orsellic acid. Orsellesic acid.* (Stenhouse, Phil. Trans. 1848, p. 66; Phil. Mag. [3] xxxii. 300; Proc. Roy. Soc. xii. 263).—This acid is produced: 1. By boiling lecanoric, α-orsellic, or β-orsellic acid with water, alcohol, or alkalis:

$$C^{16}H^{14}O^7 + H^2O = 2C^8H^8O^4.$$

2. From erythric acid (erythrin), simultaneously with picro-erythrin, when the barium- or calcium-salt of that acid is boiled with water:

$$\underset{\text{Erythric acid.}}{C^{28}H^{30}O^{14}} + H^2O = \underset{\text{Picroerythrin.}}{C^{12}H^{16}O^7} + \underset{\text{Orsellinic acid.}}{2C^8H^8O^4}.$$

3. From evernic acid, simultaneously with everninic acid, by boiling with baryta-water:—

$$\underset{\text{Evernic acid.}}{C^{17}H^{16}O^{7}} + H^{2}O = \underset{\text{Everninic acid.}}{C^{9}H^{10}O^{4}} + \underset{\text{Orsellinic acid.}}{C^{8}H^{8}O^{4}}.$$

To prepare the acid, lecanoric acid suspended in water is carefully neutralised with lime or baryta, and the liquid is boiled, care being however taken not to continue the boiling too long, as otherwise the orsellinic acid will be resolved into carbonic anhydride and orcin. The calcic or barytic orsellinate, being much more soluble than the lecanorate, dissolves in the liquid, and on adding hydrochloric acid to the solution, orsellinic acid is deposited as a gelatinous precipitate, which may be purified by crystallisation from water or alcohol.

Orsellinic acid forms colourless, prismatic crystals much more soluble in *water* and *alcohol* than lecanoric acid; it is also soluble in *ether*. The aqueous solution has a slightly rough and bitter taste and reddens litmus. When boiled for some time, it gives off carbonic anhydride and leaves orcin: $C^{8}H^{8}O^{4} = C^{7}H^{8}O^{2} + CO^{2}$. *Chloride of lime* imparts to it a very fugitive red-brown or violet tint. With *bromine* it forms tribromorcin. (Hesse.)

The orsellinates of the alkali-metals and alkaline earth-metals are soluble in water; in presence of excess of base they are easily resolved into orcin and a carbonate.—The *barium-salt*, $C^{8}H^{7}BaO^{4}$ or $C^{16}H^{14}Ba''O^{8}$, is very soluble in water and in alcohol, and is deposited therefrom in four-sided prisms. It is obtained by adding caustic baryta to an alcoholic solution of orsellinic acid, keeping the acid in excess to avoid decomposition. The liquid is then concentrated to a syrup, the acid is saturated, and the liquid left to crystallise.

**ORSELLINIC ETHERS.** These compounds are produced by boiling lecanoric or erythric acid with the corresponding alcohols.

1. *Methylic Orsellinate*, $C^{9}H^{10}O^{4} = C^{8}H^{7}(CH^{3})O^{4}$, crystallises from boiling water in silky needles, volatile without decomposition, more soluble than the ethylic ether, which it resembles in its chemical characters. (Stenhouse.)

2. *Ethylic Orsellinate*, $C^{10}H^{12}O^{4} = C^{8}H^{7}(C^{2}H^{5})O^{4}$.—This compound, called also *Orsellic*, *Lecanoric*, and *Erythric ether*, was discovered in 1830 by Heeren (Schw. J. lix. 341) who called it *pseudo-erythrin;* and has been further examined by Liebig (Pogg. Ann. xxi. 32), Kane (Phil. Trans. 1840, pp. 237, 279), Schunck (Ann. Ch. Pharm. xli. 160; lxi. 72), Rochleder and Heldt, *ibid.* xlviii. 5), Stenhouse (*loc. cit.*), Strecker (Ann. Ch. Pharm. lxviii. 111), and Hesse (*ibid.* cxvii. 297). It is obtained by prolonged boiling of an alcoholic solution of lecanoric, α-orsellic, β-orsellic, or erythric acid, or by repeatedly exhausting *Roccella tinctoria*, or other colour-yielding lichens with boiling alcohol, evaporating the united liquids to dryness, and boiling the residue with water. It separates from the aqueous or alcoholic solution in crystalline scales or needles, the mother-liquor retaining a large quantity of orcin: it may be purified by recrystallisation from boiling water. Another mode of preparing it is to pass hydrochloric acid gas in excess into a warm saturated alcoholic solution of lecanoric acid, evaporate over the water-bath to expel the greater part of the hydrochloric acid, and treat the residue with water. Orsellinic ether is then precipitated as a blackish-green resinous mass which may be purified as above.

Ethylic orsellinate forms snow-white, very thin laminæ or needles, nearly insoluble in cold water, very soluble in alcohol and ether, as well as in alkaline solutions, whence it is precipitated by acids in its original state. The aqueous solution is neutral to test-paper. It quickly turns brown, especially when dissolved in a fixed alkali. The ammoniacal solution assumes a wine-red colour when exposed to the air. It melts without loss of water, at a temperature above 120° (Heeren); at 104·5° (Kane); and solidifies to a crystalline mass at 127·5° (Hesse); when heated in water, it melts at 100°. It may be sublimed without decomposition.

Ethylic orsellinate dissolves in caustic *alkalis*, also, according to Hesse, in hot aqueous *carbonate of sodium*, and is reprecipitated by acids in the crystalline state. When boiled with *alkalis*, it gives off alcohol and yields orcin; with caustic *baryta*, a precipitate of barytic carbonate is formed.

The ether dissolves easily in strong *sulphuric acid*, and is reprecipitated by water in its original state: the solution turns brown when boiled. *Nitric acid* converts it into oxalic acid (Schunck), and if the oxidation be carefully conducted, a crystalline body is likewise formed, which melts at 60°, and appears to consist of $C^{5}H^{10}O^{6}$ (Hesse). With *bromine* and *chlorine*, orsellinic ether form substitution-products. (Hesse.)

Ethylic orsellinate does not precipitate the aqueous solutions of *mercuric chloride*, *cupric sulphate* or *neutral acetate of lead*, but forms with the *basic acetate* a copious precipitate containing, according to Kane, 80·6 per cent. lead-oxide, approximately with the formula $C^{10}H^{12}O^{4}.4Pb''O$.

*Ethylic Dichlororsellinate*, $C^8H^5Cl^2(C^2H^5)O^4$, obtained by the action of chlorine on an ethereal solution of ethylic orsellinate, crystallises in thin prisms, melts at 162°, and solidifies at 159·5°. (Hesse.)

*Ethylic Dibromorsellinate*, $C^8H^5Br^2(C^2H^5)O^4$, prepared in like manner, melts at 144°, solidifies at 138°, and forms with neutral acetate of lead, a white precipitate containing $C^{10}H^8Br^2Pb''O^4$. (Hesse, Stenhouse.)

3. *Amylic Orsellinate.* On boiling dried erythric acid with amylic alcohol for several hours, and removing the excess of alcohol by distillation, the residue yielded on standing, a mass of lustrous flaky crystals contaminated with resinous matter from which it could not be separated. (Stenhouse.)

**ORTHITE.** *Allanite. Cerin.*—A silicate of aluminium, iron, cerium, yttrium, &c., occurring in granite, gneiss, syenite and granular limestone, in Sweden, Norway, Greenland, the Ural, some parts of Germany, and several localities in the United States. The varieties containing yttrium were formerly called orthite, the rest allanite, and those among the latter which were very rich in iron, were further distinguished as cerin, but as these differences of composition arise merely from the mutual replacement of isomorphous constituents, and have no effect on the crystalline form, they are now regarded as unessential, and the name orthite is extended to the whole group.

The crystals of orthite are monoclinic prisms, homœomorphous with epidote. Ratio of axes, $a : b : c = 0·56137 : 1 : 0·8902$. Angle of inclined axes = 65° 5′. The crystals are either long and slender, or flat tabular. Twins occur like those of epidote. Cleavage parallel to oP in traces. It occurs also massive and in grains. Hardness = 5·5—6. Specific gravity = 3·3—4·2. Lustre submetallic and pitchy or resinous, occasionally vitreous. Colour pitch-brown, brownish-black or yellowish. Subtranslucent to opaque. Fracture uneven or subconchoïdal. Brittle. Before the blowpipe most orthites swell up and fuse, with ebullition, to dark-coloured tumefied glasses. With fluxes they give the reactions of iron, manganese and silica. Most of them are decomposed by acids, forming a jelly; some, however, resist the action of acids altogether.

*Analyses: a. Allanite* from Bygdin-Vand on Jotunfjeld, Norway. Black: specific gravity = 3·53—3·54; pyrognomic (that is, exhibits incandescence when heated); decomposed by acids (Scheerer, *De fossilium Allanite, Orthite, Cerin, Gadolinitque, dissertatio.* Berol. 1849).—*b. Allanite* from Snarum in Norway. Brownish-black: specific gravity = 3·79: undecomposible by acids (Scheerer).—*c. Cerin* from Riddarhyttan, Sweden. Specific gravity 3·77—3·80. Undecomposible (Scheerer).—*d. Uranorthite* from Miask in the Ural. Black: specific gravity = 3·647. Decomposible (Rammelsberg, *Mineralchemie*, p. 747).—*e.* So-called *Bucklandite.* Specific gravity = 3·48—3·66 (Hermann, J. pr. Chem. xxiii. 273; xliii. 35, 99).—*f.* From the Thuringerwald; partly crystallised in the form of epidote. Black. Specific gravity = 3·79. Undecomposible (Credner, Pogg. Ann. lxxix. 144).—*g.* From Wernheim, Baden, in syenite. Specific gravity = 3·44—3·47. Undecomposible (Stifft, *Rammelsberg's Mineralchemie*, p. 746).—*h.* Berks Co. Pennsylvania. Specific gravity = 3·782. Decomposible (Genth, J. pr. Chem. lxiv. 471).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* |
|---|---|---|---|---|---|---|---|---|
| Silica | 34·92 | 34·88 | 32·06 | 34·08 | 32·46 | 37·55 | 32·79 | 32·89 |
| Alumina | 15·90 | 15·95 | 6·49 | 16·86 | 18·09 | 15·99 | 14·67 | 12·50 |
| Ferric oxide | . . | . . | 25·26 | 7·35 | . . | . . | . . | 7·33 |
| Ferrous oxide | 14·98 | 15·35 | . . | 7·90 | 13·84 | 16·83 | 14·71 | 9·02 |
| Manganous oxide | 1·27 | . . | . . | . . | . . | 0·23 | . . | 0·25 |
| Cerous oxide | 13·34 | 13·73 | 23·80 | 21·38 | 6·77 | 3·19 | 22·31 | 15·67 |
| Oxides of Lanthanum and Didymium | 5·80 | 7·80 | 2·45 | | 9·76 | 9·30 | | 10·10 |
| Yttria | . . | . . | . . | . . | 1·50 | 0·56 | 2·42 | . . |
| Lime | 11·96 | 11·50 | 8·08 | 9·28 | 13·18 | 13·60 | 9·68 | 7·12 |
| Magnesia | 0·93 | 0·66 | 1·16 | 0·95 | 1·02 | 0·22 | 1·20 | 1·77 |
| Water | 0·51 | . . | 0·60 | 1·32 | 3·40 | 1·80 | 2·67 | 2·49 |
| | 99·61 | 99·87 | 99·99 | $Cu^2O$ 0·13 | 100·00 | 99·27 | $Na^2O$ 0·34 | 0·09 |
| | | | | 99·25 | | | $K^2O$ 0·41 | 0·14 |
| | | | | | | | 101·20 | 99·37 |

These analytical results may be represented by the general formula $3M''^2SiO^4.(Al''; Fe''')^2Si^3O^{12}$ (M″ denoting diatomic iron, cerium, yttrium, calcium, &c.), both terms of which are orthosilicates.

*Xanthorthite* is a yellowish variety of orthite, of specific gravity 2·78—2·79, and containing much water.

*Pyrorthite* is an impure variety from the neighbourhood of Fahlun in Sweden, containing bitumen. Berzelius found in it 10·43 silica, 3·59 alumina, 6·08 ferrous oxide, 1·39 manganous oxide, 13·92 cerous oxide, 4·87 yttria, 1·81 lime, 26·50 water, and 31·41 carbon (by loss). It is probably the residue of decomposition of an orthite.

*Bagrationite* from Achmatowsk, having the form of Bucklandite (epidote, ii. 490), hardness 6·5, and specific gravity 3·46, and containing 38·88 per cent. silica, 20·19 alumina, 9·82 ferric oxide, 3·82 ferrous oxide, 3·60 protoxide of cerium, lanthanum, and didymium, 17·37 lime, 1·98 magnesia, and 1·60 water (= 97·26), is composed, according to Hermann (Jahresb. 1862, p. 730), of 5 molecules of bucklandite (epidote), and 1 molecule of uralorthite, crystallised together.

A mineral called *Bucklandite*[*] from Laach in the Eifel, has been shown by v. Rath (Jahresb. 1863, p. 814) to have the form and composition of orthite; it contains 31·83 per cent. silica, 13·66 alumina, 17·95 ferrous oxide, 0·40 manganous oxide, 20·89 cerous oxide, 11·46 lime, and 2·70 magnesia (= 98·89).

A black-brown mineral resembling orthite, of specific gravity 3·44, and hardness between fluorspar and apatite, contains, according to Michaelson (Jahresb. 1863, p. 815), 29·21 per cent. silica, 2·81 alumina, 6·42 ferric oxide, 5·44 zirconia, 4·27 glucina, 9·79 cerous oxide, 15·60 oxides of lanthanum and didymium, 1·63 yttria, 14·93 lime, 0·45 magnesia, 2·45 soda, and 5·50 water.

**ORTHO-CARBONATE OF ETHYL.** $(C^2H^5)^4CO^4$. (H. Bassett, Chem. Soc. J. xvii. 198.)—This ether is produced by the action of sodic ethylate on chloropicrin:

$$CNO^2Cl^3 + 4C^2H^5NaO = 3NaCl + NaNO^2 + (C^2H^5)^4CO^4.$$

To prepare it 40 grms. of chloropicrin are heated with 300 grms. of absolute alcohol to the boiling point of the latter; 24 grms. of sodium are added by small portions; and as soon as the reaction is finished, the alcohol is distilled off and water added to the residue. Ethylic orthocarbonate then rises to the surface as an oil which must be washed with water, dried by chloride of calcium, and purified by fractional distillation.

Ethylic ortho-carbonate has a peculiar aromatic odour, specific gravity = 0·925, and boils at 158°—150°. Vapour-density obs. = 6·80; calc. = 6·65. It is decomposed by alcoholic potash at the boiling heat, yielding a considerable quantity of potassic carbonate. When digested for some hours with boric anhydride, it yields acid ethylic borate (i. 650) and diethylic carbonate:

$$(C^2H^5)^4CO^4 + 2B^2O^3 = (C^2H^5)^2B^4O^7 + (C^2H^5)^2CO^3.$$

**ORTHOCLASE.** See Felspar (ii. 619).

**ORTHO-SALTS.** The prefixes *ortho* and *meta* have been introduced by Odling to denote two classes of salts of the same acid, which differ from one another by one or more molecules of metallic oxide, $M^2O$, $M''O$, &c., the more basic salts being called ortho- and the less basic, meta-salts, as in the following examples:—

*Borates.*

| | | | |
|---|---|---|---|
| Orthoborate of Sodium | $Na^3BO^3$ | Orthoborate of Lead | $\ddot{Pb}{}^3B^2O^6$ |
| Metaborate | $NaBO^2$ | Metaborate | $Pb''B^2O^4$ |
| Difference | $Na^2O$ | Difference | $2Pb''O$ |

*Carbonates.*

| | | | |
|---|---|---|---|
| Orthocarbonate of Ethyl | $(C^2H^5)^4CO^4$ | Orthocarbonate of Calcium | $\overset{''}{Ca}{}^2CO^4$ |
| Metacarbonate | $(C^2H^5)^2CO^3$ | Metacarbonate | $Ca''CO^3$ |
| Difference | $(C^2H^5)^2O$ | Difference | $Ca''O$ |

*Nitrates.*

| | | | |
|---|---|---|---|
| Orthonitrate of Mercurosum | $\left.\begin{matrix}Hg^2\\H\end{matrix}\right\}NO^4$ | Orthonitrate of Copper | $\overset{''}{Cu}{}^3N^2O^8$ |
| Metanitrate | $HgNO^3$ | Metanitrate | $Cu''N^2O^6$ |
| Difference | $HgHO$ | Difference | $2Cu''O$ |

Orthonitrate of Bismuth . . $Bi'''NO^4$ = $\overset{'''}{Bi}{}^3N^3O^{12}$
Metanitrate . . . . . . . $Bi'''N^3O^9$
Difference $\overset{'''}{Bi}{}^2O^3$

*Phosphates.*

| | | | |
|---|---|---|---|
| Orthophosphate of Sodium | $Na^3PO^4$ | Orthophosphate of Barium | $\overset{''}{Ba}{}^3P^2O^8$ |
| Metaphosphate | $NaPO^3$ | Metaphosphate | $Ba''P^2O^6$ |
| Difference | $Na^2O$ | Difference | $2Ba''O$ |

See Borates (i. 640), Carbonates (i. 778), Nitrates (iv. 82), Phosphates, Silicates, &c.

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[*] This name having been applied both to orthite and to a variety of epidote is best given up altogether.

**ORTHOSE.** Syn. with Orthoclase.

**OSMAN-OSMIC ACID.** Syn. with Osmiamic Acid.

**OSMAZOME** (from ὀσμή odour, and ζωμός broth). A name applied by Thénard to that portion of the aqueous extract of meat which is soluble in alcohol and contains those constituents of the flesh which determine its taste and smell.

**OSMELITE.** Syn. with Pectolite.

**OSMIAMIC ACID.** $H^2Os^2N^2O^5$.—This acid, discovered by Fritzsche and Struve (J. pr. Chem. xli. 97), is produced by the action of ammonia on osmic tetroxide in presence of fixed bases. The potassium-salt, $K^2Os^2N^2O^5$, is obtained by adding ammonia to a hot solution of the tetroxide in excess of potash; the deep orange colour of the liquid then changes to light yellow, and the potassium-salt separates as a yellow crystalline powder, which may be purified by recrystallisation from the least possible quantity of boiling water. The reaction is:

$$6OsO^4 \quad + \quad 8NH^3 \quad + \quad 6KHO \quad = \quad 3K^2Os^2N^2O^5 \quad + \quad N^2 \quad + \quad 15H^2O.$$

The potassium-salt may be converted into the silver-salt by precipitation, and from this the aqueous acid may be prepared by decomposition with hydrochloric acid. It may be kept for some days when dilute, but soon decomposes in the concentrated state. It is a strong acid, decomposing not only the carbonates but even the chlorides of potassium and sodium.

Osmiamic acid is dibasic, its salts having the composition $M^2Os^2N^2O^5 = M^2O.Os^2N^2O^4$. Fritzsche and Struve regard the anhydride $Os^2N^2O^4$ (not isolated) as a compound of $OsN^2$ with $OsO^4$, and call it osman-osmic acid. Gerhardt (Compt. chim. 1847, p. 304), who suggested the name osmiamic acid, supposes the salts to contain 1 at. oxygen more than in the formula above given, regarding therefore the hypothetical anhydride as $Os^2N^2O^5$, and representing its formation (in the salts) by the equation $2OsO^4 + 2NH^3 = Os^2N^2O^5 + 3H^2O$; but Fritzsche and Struve's formula agrees best with the composition and reactions of the salts.

The osmiamates of the alkali- and alkaline earth-metals are soluble in water; the lead, mercury, and silver salts are insoluble. The *ammonium-salt*, $(NH^4)^2Os^2N^2O^5$, forms large yellow crystals isomorphous with those of the potassium-salt, easily soluble in water and alcohol, and detonating at 125°. The *barium-salt*, $Ba''Os^2N^2O^5$, crystallises in yellow, shining needles, moderately soluble in water and detonating at about 150°. The *lead-salt*, $Pb''Os^2N^2O^5.Pb^2O$ ?, obtained by mixing an alcoholic solution of the potassium or ammonium salt with nitrate of lead, is a yellow, crystalline precipitate which becomes dark-coloured during washing. The *mercuric salt*, obtained by decomposing the silver-salt with mercuric chloride, forms prismatic easily decomposible crystals. The *mercurous-salt* is a light yellow amorphous precipitate which volatilises quickly when heated.

The *potassium-salt*, $K^2Os^2N^2O^5$, crystallises in yellow dimetric octahedrons with terminal angles of 106° 16′ and lateral angles of 116° 5′. It is much less soluble in alcohol than in water, insoluble in ether; may be heated to 180° without alteration, but detonates at higher temperatures. Heated with hydrochloric acid and chloride of potassium, it gives off chlorine and is converted into potassio-osmioso-osmic chloride (chlorosmite of potassium) (Claus):

$$K^2Os^2N^2O^5 \; + \; 4KCl \; + \; 18HCl \quad = \quad 2(3KCl.OsCl^3) \; + \; 2NH^4Cl \; + \; 5H^2O \; + \; Cl^8.$$

The *silver-salt*, $Ag^2Os^2N^2O^5$, obtained by precipitation, or by dissolving osmic tetroxide in an ammoniacal solution of the silver-salt and supersaturating with nitric acid, is a lemon-yellow crystalline powder, very slightly soluble in water and in cold nitric acid, easily soluble in ammonia. It blackens when exposed to light, detonates violently at 80°, also by percussion, or when sulphydric acid gas is passed over it.

The *sodium-salt* is very soluble and crystallises from a syrupy solution in rather large prismatic hydrated crystals.

The *zinc-salt* is very soluble.

An *ammoniacal zinc-salt*, $4NH^3.Zn''Os^2N^2O^5$, separates on mixing an ammoniacal solution of osmic tetroxide with a zinc-salt, as a light yellow crystalline powder, permanent in the air, easily decomposible by water, nearly insoluble in ammonia. Cadmium forms a similar salt.

**OSMIAMIDE.** The name given by Frémy to the compound $N^2H^4(OsO^2)''$, which he supposes to exist in combination with sal-ammoniac in the yellow substance produced by digesting osmite of potassium in a cold solution of sal-ammoniac (pp. 244, 246).

**OSMIC ACID.** }
**OSMIOUS ACID.** } See Osmium, Oxides of (pp. 245, 246).

**OSMIRIDIUM** or *Iridosmine*.—The native alloy of iridium and osmium, occurring together with platinum, &c. in various localities. Its composition and properties have been already given under IRIDOSMINE (iii. 325), and several methods of decomposing it under IRIDIUM (iii. 314). The following are additional methods:—*a.* 90 grms. of the ore are mixed with 180 grms. saltpetre and 90 grms. caustic potash, and the mixture is exposed in separate portions to a strong red heat for an hour or an hour and a half in a large silver crucible, placed within a hessian crucible containing magnesia, each melted portion being poured out into an iron dish and the still undecomposed residue heated twice or thrice more with the same quantity of flux, before a fresh portion of the original mixture is introduced into the crucible. The cooled and pulverised mass is then introduced into a vessel which can be closed, and briskly agitated for four hours in a dark place with 14 litres of distilled water, and the clear deep orange-coloured solution (*A*) is decanted from the black sediment (*B*) which latter is washed with water in a funnel plugged with asbestos. The solution *A* smells slightly of osmic tetroxide, and contains free potash, nitrite, osmite, ruthenate and nitrate of potassium, together with a small quantity of osmic tetroxide; no other platinum-metal. The residue *B* is a velvet-black, somewhat crystalline powder, consisting principally of iridic oxide and acid iridiate of potassium, with portions of ruthenic sesquioxide, osmic dioxide, ferric oxide, and traces of cupric and palladic oxides, all soluble in acids; also of a residue insoluble in acids consisting of oxides of iridium, platinum, and rhodium, with a certain quantity of undecomposed ore.

To extract the ruthenium, *B* is fused a second time with the fluxes above mentioned; the solution obtained by treating the fused mass with water is added to *A*; and the still undissolved residue to *B*. The solution is next neutralised with very dilute nitric acid, whereby a black precipitate *b* is thrown down; the clarified solution *a* is decanted, and the precipitate consisting chiefly of osmic hydrate, $OsO^2.2H^2O$, containing from 15 to 20 per cent. ruthenic sesquioxide, is washed. To separate the metals, this precipitate is introduced into a large retort fitted with a luted and well-cooled receiver, together with 2 lbs. hydrochloric and 3 lbs. nitric acid, and slowly and carefully distilled till the greater part of the acid has passed over, and the residue in the retort has become viscid. This residue consists chiefly of ruthenic tetrachloride, $RuCl^4$, with a small quantity of trichloride. (For the method of obtaining the metal from it, see RUTHENIUM.)

The faintly yellowish solution *a* still contains oxides of ruthenium together with a large quantity of osmic tetroxide. It is distilled with 2 lbs. of hydrochloric acid till all the osmic tetroxide has passed over, and the residue in the retort has become rose-coloured (from formation of red ruthenic chloride); the red liquid is concentrated; the greater part of the potassic nitrate crystallised out; the concentrated solution then evaporated to dryness; the residue dissolved; and the ruthenium precipitated from the solution by sulphide of ammonium, with addition of a little free acid. The osmic tetroxide obtained at the same time may be separated by fractional distillation; or the solution containing it, may be treated according to Frémy's method (Ann. Ch. Phys. [3] xii. 521), by mixing it with caustic potash and a little alcohol, and adding pulverised sal-ammoniac. The greater part of the osmium is then thrown down in the form of a compound of osmiamic acid with sal-ammoniac.

The powder *B*, which contains considerable quantities of ruthenium and osmium, is distilled with excess of nitromuriatic acid till the whole of the osmic tetroxide has passed over; and the residual liquid is strongly concentrated and left to cool, whereupon it deposits the greater part of the iridium as black chloriridiate of potassium, $K^2Ir^{iv}Cl^6$. The mother-liquor, after filtration, is mixed with a little sal-ammoniac to throw down the rest of the iridium; filtered after standing from the crystalline precipitate of chloriridiate of ammonium; and the liquid is then mixed with a large quantity of powdered sal-ammoniac. The resulting brown crystalline mass, after washing with sal-ammoniac and weak spirit, yields ruthenium in the form of the double salt, $(NH^4)^2Ru'''Cl^5$. (Claus, N. Petersb. Acad. Bull. v. 453; Jahresb. 1861, p. 322.)

*β.* The following method of treating Californian osmiridium, which contains a considerable proportion of ruthenium, is given by Gibbs (Sill. Am. J. [2] xxxi. 53). The ore is first freed from silica and other impurities by fusion with 3 pts. dry carbonate of sodium, and subsequent lixiviation; 1 pt. of it is then fused with 1 pt. caustic potash and 2 pts. saltpetre; and the cooled mass broken into lumps is boiled with water containing $\frac{1}{10}$ of its bulk of strong alcohol, till completely disintegrated. The liquid together with the lighter particles of oxide is then decanted, and the residue is again treated with water and decanted after standing for some time. There is thus obtained a solution of potassic osmite, a large quantity of black oxides (probably a mixture of $RuO^2$, $Ru^2O^3$, or their hydrates) and a coarse heavy powder chiefly consisting of undecomposed ore. The latter is again fused with hydrate and nitrate of potassium, and the melted mass treated as above. The solution containing the potassic osmite and the salts of the alkali-metals is decanted from the deposited black oxides still containing osmium; and these oxides, after washing with hot water and alcohol, are introduced into a capacious retort provided with a safety-tube and connected with a tight-fitting cooled receiver, which again is connected by wide tubes with two or three Woulfe's bottles containing a strong solution of potash and a little alcohol. A large excess of strong hydrochloric acid is then cautiously poured through the safety-tube into the retort, and after the first violent action, which causes a part of the osmic tetroxide to distil over spontaneously, is over, the distillation is continued at the heat of a sand-bath till no more osmic tetroxide collects in the neck of the retort, and that which is previously condensed flows out in oily drops. At the end of the distillation the retort is left to cool; the receiver is disconnected from it and closed by a cork, and the osmic tetroxide is driven over by a moderate heat into the Woulfe's bottles; and the contents of these vessels are mixed with the solution obtained by lixiviating the original fused mass. The liquid evaporated over the water-bath yields on cooling crystals of potassic osmite. The mother-liquor contains only traces of osmium and is worthless.

The dark brown solution poured out from the retort is evaporated to dryness, the residue is redissolved in hot water; the solution is evaporated again after addition of a little hydrochloric acid; this process is repeated till the odour of osmic tetroxide is no longer perceptible; and a cold saturated solution of chloride of potassium is then added, which dissolves the chlorides of iron and palladium, while platinum, iridium, rhodium, and ruthenium remain as double salts insoluble in a strong solution of chloride of potassium. The latter are well washed with a saturated solution of potassic chloride, which removes almost all the iron and palladium, and leaves the double chlorides together with the insoluble impurities of the ore.

**OSMITOPSIS, OIL OF.** *Osmitopsis asteriscoïdes*, an aromatic plant of the composite order growing near Cape Town, yields an essential oil possessing tonic and antispasmodic properties. It is greenish-yellow, has a burning taste, and a pungent, not very agreeable odour recalling that of camphor and oil of cajeput. Specific gravity = 0·931. It reduces an ammoniacal solution of silver-nitrate on long boiling. When distilled, it begins to boil at 130°, and enters into regular ebullition between 176° and 178°, two-thirds of the oil passing over between this point and 188°; the thermometer then continues to rise till it reaches 208°, and a small quantity of camphor sublimes on the sides of the vessel. The portion collected between 178° and 182° contains 77·9 per cent. carbon and 11·79 hydrogen, agreeing nearly with the formula $C^{10}H^{18}O$, according to which oil of osmitopsis is isomeric with borneol (i. 626) and oil of cajeput (i. 712).

**OSMIUM.** *Symbol* Os. *Atomic weight* 199.—A metal belonging to the platinum group, discovered by Tennant (Phil. Trans. 1804, p. 411), and further examined by Berzelius (Pogg. Ann. xiii. 463; xv. 208 and 527), Frémy, Compt. rend. xxxviii. 1008), Claus (Ann. Ch. Pharm. lix. 234; lxiii. 341; N. Petersb. Acad. Bull. ii. 158; iv. 453; vi. 145; Jahresb. 1860, p. 204; 1861, p. 320; 1863, p. 295), Deville and Debray (Ann. Ch. Pharm. civ. 227; cxiv. 78; Ann. Ch. Phys. [3] lvi. 385; Jahresb. 1857, p. 260, 1859, p. 231), and Gibbs (Sill. Am. J. xxix. 427; xxxi. 63; Jahresb. 1860, p. 217; 1861, p. 328). The name of the metal is derived from ὀσμή (odour) on account of the strong and peculiar odour of its highest oxide.

Osmium occurs combined with iridium, forming the alloy called *osmiridium* or *iridosmine*, in native platinum, partly in distinct white metallic grains, partly intimately mixed or combined with the platinum and other metals, and remaining in black scales when those metals are dissolved in nitro-muriatic acid; osmiridium also occurs with chrome-iron in irite (iii. 325).

The separation of osmium from iridium and the other metals with which it is associated, depends chiefly on its ready oxidation by nitric or nitro-muriatic acid, or by ignition in air or oxygen-gas, and the volatility of the oxide thus produced. The methods of effecting the separation have been already described under IRIDIUM (iii. 314—316, Nos. 1, 2, 4, 6, 7), and OSMIRIDIUM (iv. 241).

To obtain metallic osmium, the distilled osmic tetroxide is digested with hydrochloric acid and metallic mercury in a well-closed vessel at 140°. The osmium is reduced by the mercury, and an amalgam formed, which, when distilled in a retort through which hydrogen is passed till all the mercury and calomel are expelled, leaves osmium as a black powder without metallic lustre (Berzelius). Metallic osmium may also be obtained by digesting osmic tetroxide with hydrochloric acid and metallic zinc, (Vauquelin),—or by passing the vapour of the tetroxide mixed with hydrogen through a glass tube heated to redness for about an inch of its length, the osmium being there deposited as a compact metallic ring (Berzelius), or by igniting a mixture of chlorosmiate of ammonium with sal-ammoniac (Berzelius).

The following is the method adopted by Deville and Debray. A very intimate mixture of osmiridium with 5½ pts. barium-peroxide is heated for an hour or two in a well-closed earthen crucible to the melting point of silver; the resulting black mass coarsely powdered is drenched in a glass retort with a little water, and then with a mixture of 8 pts. hydrochloric and 1 pt. ordinary nitric acid; the mixture is distilled in a retort provided with a closely fitting and well cooled receiver containing aqueous ammonia, as long as vapours of osmic tetroxide continue to pass over; the osmate of ammonium thus obtained is supersaturated with sulphydric acid; the liquid containing the suspended sulphide of osmium is boiled for some time and filtered; and the sulphide of osmium is dried at a regular temperature, as it might take fire if too strongly heated. The dried sulphide is then introduced into a crucible made of gas-coke, polished on its inner surface, and fitted with a well-ground cover, and this crucible, placed within an earthen crucible containing sand and likewise well closed with a ground cover, is exposed for four or six hours to the melting heat of nickel. The sulphide of osmium is thereby reduced to the metallic state.

*Properties.*—The properties of metallic osmium vary according to the mode of preparation. In the pulverulent state it is black, destitute of metallic lustre, which however it acquires by burnishing, and has, according to Berzelius, a density of only 7; but in the compact state, as obtained by Berzelius's method above described, it exhibits metallic lustre and a density of 10. When reduced by the wet way it has a bluish tinge. It is malleable enough to bear rolling into thick plates, but is easily reduced to powder under the hammer (Berzelius). Deville and Debray, by the method just described, obtained it in easily divisible lumps having a bluish colour lighter than that of zinc. It may be reduced to a more compact state by heating it to the melting point of rhodium, when it attains a density of 21·3 to 21·4. When heated with 7 or 8 times its weight of zinc in a charcoal crucible to bright redness, it dissolves in the zinc, separates on slow cooling in the crystalline state, and remains after the zinc has been removed by hydrochloric acid, as a very hard crystalline powder. If osmium be melted with zinc and the resulting alloy treated with hydrochloric acid, the whole of the osmium remains undissolved as an amorphous very inflammable powder; but if the zinc be expelled from the alloy by a strong heat, and the remaining osmium heated in a charcoal crucible before an oxy-hydrogen blowpipe capable of melting rhodium, the osmium is obtained as a bluish metallic-shining mass, having the density of 21·4, hard enough to scratch glass, not however quite compact, but penetrated by cavities. At a still higher temperature, capable of melting ruthenium and iridium and volatilising platinum, osmium likewise volatilises, but still does not melt; it is in fact the most infusible of all metals.

Osmium in the finely divided state is highly combustible: continuing to burn when set on fire till it is all volatilised as tetroxide. In this state also it is easily oxidised by nitric or nitro-muriatic acid, being converted into tetroxide. But after exposure to a red heat, it becomes much less combustible and is not oxidised by nitric or nitro-muriatic acid (Berzelius). Osmium which has been heated to the melting point of rhodium does not give off any vapour of tetroxide when heated to the melting point of zinc, but takes fire at higher temperatures. (Deville and Debray.)

**OSMIUM, CHLORIDES OF.** Osmium forms three chlorides having the formulæ $OsCl^2$, $OsCl^3$, and $OsCl^4$. A hexchloride $OsCl^6$ is also said by Berzelius to exist in certain double salts; but its existence is not well established. There is no chloride corresponding to the tetroxide.

**Dichloride of Osmium** or **Osmious Chloride.** $OsCl^2$.—When pulverised osmium is heated in perfectly dry chlorine gas free from air, there is formed, first a blue-black sublimate of osmious chloride, then a red sublimate of osmic chloride, $OsCl^4$. (The green chloride mentioned by Berzelius is formed only when moisture is not completely excluded.) The osmious chloride, which is produced in relatively small quantity, and is difficult to obtain pure, dissolves in water with dark violet-blue colour. A similar solution may be obtained by dissolving osmious hydrate in hydrochloric acid, or by the action of reducing agents (such as zinc, tannic acid, ferrocyanide of potassium, or alcohol) on a solution of the tri- or tetra-chloride; but it is very unstable, oxidising as quickly as ferrous chloride, and changing in colour to dark red, and ultimately to yellow. The addition of chloride of potassium renders it more stable, by forming a double salt. (Claus.)

**Trichloride** or **Osmioso-osmic Chloride.** $OsCl^3$.—This compound, which is also very unstable and cannot be obtained in the free state, is contained in the solution produced by dissolving the mixture of the di- and tri-chlorides resulting from the action of chlorine on pulverised osmium, in water. The solution has at first a chrome-green or blue-green colour, but soon becomes purple-violet, from formation of trichloride, and finally colourless, in consequence of the resolution of this compound into osmic tetroxide, hydrochloric acid, and a mixture of osmious and osmic oxides which is

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thrown down in the form of a black powder. The trichloride is sometimes also formed by treating a solution of the yellow tetrachloride with a large quantity of hydrochloric acid, or by the action of sulphydric acid on a solution of osmic tetroxide containing a large quantity of hydrochloric acid.

*Potassio-osmioso-osmic chloride* or *Chlorosmite of Potassium*, $K^2OsCl^6$ or $3KCl.OsCl^3$, is produced, together with potassio-osmic chloride, when a mixture of pulverised osmium and chloride of potassium is strongly ignited in chlorine gas. On dissolving the ignited mass in water, and evaporating, the osmic salt crystallises out first, and afterwards the osmioso-osmic salt in small quantity. The latter is more easily obtained by the action of hydrochloric acid and chloride of potassium on osmiamate of potassium (p. 239): a concentrated aqueous solution of osmic tetroxide is mixed with caustic potash and ammonia, then saturated with dilute hydrochloric before it turns yellow and deposits osmiamate of potassium and quickly evaporated to dryness over the water-bath; and the residue is freed from sal-ammoniac and chloride of potassium by careful washing with ice-cold water.

The double chloride is thus obtained in dark red or red-brown crystals, $3KCl.OsCl^3.3H^2O$, which give off half their water by efflorescence in the air, becoming rose-red at the same time, and the whole between 150° and 180°. It dissolves easily, with deep cherry-red colour in water and in alcohol, but is insoluble in ether; has a nauseous strongly astringent taste, and decomposes, especially when heated, turning brown, and yielding a black oxychloride. The aqueous solution gives with *potash*, *ammonia*, or *carbonate of potassium*, a brownish-red precipitate of hydrated osmioso-osmic oxide, which dissolves in ammonia, but only partially in potash (and is precipated therefrom at the boiling heat. The same solution gives with *nitrate of silver* a dirty grey-brown precipitate soluble in ammonia. Heated with *tannic acid*, or *alcohol* (with addition of hydrochloric acid) it is reduced to the blue dichloride. With *sulphydric acid* and *sulphide of ammonium*, it yields brown-black sulphide of osmium, insoluble in sulphide of ammonium. (Claus.)

*Ammonio-osmioso-osmic Chloride.* $3NH^4Cl.OsCl^3.3H^2O$, resembles the potassium-salt.

**Tetrachloride of Osmium** or **Osmic Chloride.** $OsCl^4$.—This is the red compound which constitutes the principal part of the product obtained by igniting osmium in chlorine gas. It dissolves with yellow colour in water and alcohol, and is decomposed quickly in dilute solution, more slowly in presence of hydrochloric acid or metallic chlorides, yielding a black precipitate of osmic oxide and a solution of osmic tetroxide and hydrochloric acid.

Osmic chloride unites with the chlorides of the alkali-metals forming salts sometimes called chlorosmates. From the solutions of these salts, *sulphydric acid* and *sulphide of ammonium* slowly precipitate a yellow-brown sulphide insoluble in alkaline sulphides. *Nitrate of silver* forms an olive-green; *stannous chloride* a brown precipitate. *Tannic acid* on heating produces a blue colour, but no precipitate; *ferrocyanide of potassium*, first a green, then a blue colour; *iodide of potassium*, a deep purple-red colour. *Potash* gives a black, *ammonia* a brown precipitate, slowly in the cold, immediately on boiling. Metallic *zinc* and *formate of sodium* throw down metallic osmium. (Berzelius.)

*Ammonio-osmic Chloride* or *Chlorosmate of Ammonium*, $2NH^4Cl.OsCl^4$, is formed on mixing a solution of the sodium-salt with sal-ammoniac, as a red-brown precipitate, and separates from the mother-liquor in black-brown octahedrons. It is even more decomposible than the potassium-salt, and leaves when ignited a residue of spongy osmium. (Claus.)

*Argento-osmic Chloride.* $2AgCl.OsCl^4$.—Obtained as a dirty green precipitate on adding ammonia to the solution of the sodium-salt (Claus). In contact with ammonia it is converted into a minium-red very unstable compound, $Ag^2OsCl^6.2NH^3$, soluble with yellow colour in a large quantity of water (Eichler, Jahresb. 1860, p. 216, Claus). The same compound is formed on adding nitrate or ammonio-chloride of silver to a solution of potassio-osmic chloride containing ammonia. (Eichler.)

*Potassio-osmic Chloride.* $K^2OsCl^6$ or $2KCl.OsCl^4$, is obtained by gently igniting a mixture of chloride of potassium and metallic osmium in a stream of chlorine (Berzelius), or by precipitating a solution of the sodium-salt with chloride of potassium (Claus). It forms brown or minium-red octahedrons, sparingly soluble in water, insoluble in alcohol. Paper moistened with the aqueous solution acquires a blue colour not removable by washing (Berzelius). The aqueous solution becomes greenish after a while, and black on boiling, the osmic chloride being decomposed in the manner above mentioned. *Potash* decolorises the solution, and on boiling throws down a blue-black precipitate of osmic-hydrate. Dilute *ammonia* throws down a yellowish-white precipitate which changes after a while into a brown ammoniacal compound, $N^2H^6OsO^2$. (Claus.)

Eichler (Jahresb. 1860, p. 214), by dissolving hypo-osmite of potassium, $K^2O.3OsO^2$

(obtained by exposing an alcoholic solution of the osmite, $K^2O.Os^2O^3$ (p. 247), to sunshine), in cold hydrochloric acid, obtained a dark violet solution of potassio-osmic chloride, which was more readily decomposible than the greenish-yellow solution of the octahedral double salt above described, inasmuch as it gave with potash an *immediate* black precipitate of osmic oxide, a similar precipitate with a small quantity of ammonia, also with phosphate of sodium. By exposure to the air it was gradually converted into the yellow solution of the octahedral salt. [? Did not this violet solution contain osmious as well as osmic chloride.]

*Sodio-osmic chloride*, $2NaCl.OsCl^4$, prepared by heating a mixture of sulphide of osmium and chloride of sodium in a current of moist chlorine, crystallises in orange-coloured rhombic prisms an inch long, easily soluble in water and in alcohol. (Claus.)

**Hexchloride of Osmium.** $OsCl^6$?—Not known in the free state, but said by Berzelius to be obtained, in combination with chloride of ammonium, when a solution of osmic tetroxide mixed with ammonia is treated with hydrochloric acid, mercury being also placed in contact with it. After a few days the liquid loses the odour of osmic tetroxide, and leaves the double chloride on evaporation in brown dendritic crystals.

**OSMIUM, DETECTION AND ESTIMATION OF.** All osmium-compounds, when boiled with an excess of nitric acid, give off the unpleasant pungent odour of osmic tetroxide. By ignition in hydrogen gas, they are reduced to metallic osmium, which as well as the lower oxides, emits the same odour when heated in contact with the air. Those which contain iridium, however, offer greater resistance to the action of oxygen or oxidising agents than those which are free from that metal. Such compounds should first be reduced by hydrogen to the state of an alloy of osmium and iridium, in which state small quantities of osmium are more easily detected by oxidation.

For the reactions of osmium salts in solution, see pp. 243, 246.

*Quantitative Estimation and Separation.* Osmium is generally estimated in the metallic state. The best mode of separating it from the metals with which it is usually accompanied, is to volatilise it in the form of osmic tetroxide—by distillation with nitromuriatic acid, if the compound be perfectly soluble therein, or by roasting in a stream of oxygen—receiving the vapours of osmic acid in a strong solution of potash; and to reduce the resulting salt, by the addition of a few drops of alcohol, to osmite of potassium, which is insoluble in the alcoholic liquor. The osmite of potassium is then digested in a cold solution of sal-ammoniac, whereby the compound $2NH^4Cl.N^2H^4OsO^2$ is produced, and the osmium reduced to the metallic state by igniting this last-mentioned compound in a current of hydrogen gas. (Frémy.)

Another mode of proceeding is to condense the acid vapours evolved by distilling a compound of osmium with nitro-muriatic acid in a well-cooled receiver, and precipitate the osmium from the solution by metallic mercury. A precipitate is thereby obtained consisting of calomel, a pulverulent amalgam of osmium, and metallic mercury containing a very small quantity of osmium. This mixture is heated in a glass bulb through which a stream of hydrogen is passed, whereupon the mercury and its chloride volatilise, and metallic osmium is left in the form of a black powder. The liquid, however, still retains a small quantity of osmium, which may be isolated by saturating with ammonia, evaporating to dryness, and calcining the residue (Berzelius). The osmium may also be precipitated from the distilled liquid by sulphydric acid, the solution, after complete saturation, being left for several days in a stoppered bottle, till the sulphide of osmium is completely deposited. The sulphide is then washed, dried, and weighed; but as it is apt to retain moisture, and, moreover, oxidises to a certain extent in the air, the method is not very exact. It is recommended, however, for the estimation of small quantities of osmium, the method of precipitation by mercury being better adapted for larger quantities.

The most difficult of all compounds of osmium to decompose is the native alloy of osmium and iridium, especially the pale variety. The difficulty arises in a great measure from the extreme hardness of the mineral. The best method of disintegrating it is that given by Deville and Debray, which consists in igniting it with six times its weight of pure zinc, till the latter is completely volatilised. The osmiridium is then left behind as a spongy mass, easily reduced to very fine powder. The decomposition may then be effected by igniting the pulverised mineral mixed with chloride of sodium in a stream of chlorine (Wöhler); or by ignition with nitrate and hydrate of potassium (Claus); or with chlorate and hydrate of potassium (Fritzsche and Struve, J. pr. Chem. xxxvii. 483); or with peroxide and nitrate of barium (Deville and Debray). See IRIDIUM (iii. 314) and OSMIRIDIUM (iv. 241).

*Atomic weight of Osmium.*—Berzelius determined the atomic weight of this metal by heating potassio-osmic chloride, $2KCl.OsCl^4$, in a current of hydrogen, 1·3165 grm. of the salt leaving 0·401 grm. KCl and 0·535 grm. osmium; hence, if KCl = 174·5, we find Os = 198·8.

Different numbers are however obtained by comparing the original weight of the salt with that of the chloride of potassium left, or with the quantity of chlorine given off (0·3805 grm.), the result being in the former case, Os = 198·4; in the latter, Os = 200·32.

Frémy (Ann. Ch. Phys. [3] xii. 361), from experiments with osmic tetroxide, the details of which have not been published, estimates the atomic weight of osmium at 199·6.

The number 199 may therefore be regarded as very near the truth.

**OSMIUM, OXIDES OF.** Five oxides of osmium are known, namely $OsO$, $Os^2O^3$, $OsO^2$, $OsO^3$, $OsO^4$.—The first three form salts with acids; the third appears also to act as a weak acid forming a potassium-salt; the fourth is also a weak acid forming with bases a few salts called osmites. The tetroxide, $OsO^4$, is usually regarded as an acid and called osmic acid; but its solutions in alkalis are very unstable and do not yield definite salts: hence it cannot be regarded as a true acid oxide.

**Protoxide,** or **Osmious Oxide.** $OsO$.—Obtained in the anhydrous state by igniting osmious or potassio-osmious sulphite in a stream of carbonic anhydride. A blue-black hydrate, probably $OsH^2O^2$, is produced by heating osmious sulphite with strong potash solution, in a closed vessel. When recently prepared it forms with hydrochloric acid a blue solution which however quickly becomes violet, dark-red, and finally yellow, oxidising in fact as quickly as a solution of a ferrous salt (Claus). Berzelius by precipitating potassio-osmious chloride with potash, obtained a greenish-black hydrate which dissolved slowly in acids, forming green solutions.

*Osmious sulphite*, $OsSO^3$, is obtained by mixing an aqueous solution of the tetroxide with sulphurous acid. The liquid then turns yellow, red and finally deep indigo-blue, and when evaporated or heated with sulphate or carbonate of sodium, deposits the salt as a blue jelly, which easily oxidises while moist, but forms, when dry, a very stable powder of a dull black-blue colour. The salt is insoluble in water, but dissolves in hydrochloric acid with indigo-blue colour, and without evolution of sulphurous anhydride. It is decomposed by potash at the boiling heat, and is resolved by heat into sulphide of osmium, osmic tetroxide and sulphurous acid, the two latter of which however easily reproduce the original salt. (Claus.)

*Potassio-osmious Sulphite.* $3K^2SO^3.OsSO^3.5H^2O$ or $\left.\begin{matrix}(\overset{\prime\prime}{S}O)^4\\ Os''.K^6\end{matrix}\right\}O^8.5H^2O$.—Potassio-osmic chloride heated with aqueous sulphurous acid becomes colourless and deposits this salt as a white pulverulent precipitate, which when dried forms a light crystalline powder having a tinge of rose-colour. It dissolves slightly in water, and has a scarcely perceptible lustre; decomposes at 180°, assuming a dingy violet colour. (Claus, Ann. Ch. Pharm. xiii. 355.)

*Acid Osmious Sulphite with Chloride of Potassium.* $6KCl.OsSO^3.SO^2$.—Formed by treating the last-described salt with hydrochloric acid. It is a brown-red crystalline anhydrous salt, very soluble and having a sharp taste. (Claus, Ann. Ch. Pharm. lxvii. 375.)

**Sesquioxide of Osmium,** $Os^2O^3$, is obtained by heating either of the double salts of the trichloride (p. 244) with carbonate of sodium in a stream of carbonic anhydride. It is a black powder insoluble in acids. The *hydrate*, $Os^2O^3.3H^2O$? obtained by precipitation, has a dirty brown-red colour, is soluble in acids, but does not yield pure salts.

**Dioxide,** or **Osmic Oxide,** $OsO^2$, is obtained as a black insoluble powder, by heating potassio-osmic chloride (p. 245) with carbonate of sodium in a stream of carbonic anhydride (Berzelius, Claus), or in copper-red metallic-shining lumps, by heating the corresponding hydrate. *Osmic hydrate*, $OsO^2.2H^2O$, is obtained by precipitating a solution of potassio-osmic chloride with potash, at the boiling heat (Berzelius, Claus), or in greater purity by mixing a solution of potassic osmite ($K^2O.OsO^3$) with dilute nitric acid (Claus):

$$2OsO^3 \quad = \quad OsO^2 \quad + \quad OsO^4.$$

It is then precipitated as a black somewhat gummy powder, which dries up to lumps having a conchoïdal fracture. It is sparingly soluble in acids, and when heated, decomposes with scintillation, giving off osmic tetroxide and hydrogen, and leaving osmic oxide:

$$2OsH^4O^4 \quad = \quad OsO^2 \quad + \quad OsO^4 \quad + \quad H^4 \quad + \quad 2H^2O.$$

Claus supposes that there is also another osmic hydrate, $OsO^2.5H^2O$, which is soluble in potash, and is converted by heat into the preceding hydrate.

The anhydrous oxide and the hydrate are both insoluble in acids. An *osmic sulphate* is said to be obtained by dissolving disulphide of osmium in cold dilute nitric acid; but the only well-defined osmic salts known are the double salts of osmic chloride with the chlorides of the alkali-metals (p. 245).

A compound of osmic oxide with potash, $K^2O.3OsO^2$, which may be called *hypo-osmite of potassium*, is obtained, according to Eichler (p. 245) by exposing a solution of osmic tetroxide mixed with alcohol and excess of potash to direct sunshine, and treating the black precipitate which separates after a while with dilute nitric acid.

**Trioxide of Osmium.** *Osmious Anhydride.* $OsO^3$.—This oxide is not known in the free state, but according to Mallett (Sill. Am. J. [2] xxix. 49), when the mass obtained by fusing platinum-residues with 3 pts. saltpetre is distilled with strong sulphuric acid, a mixture or compound of the trioxide with the tetroxide passes over at the beginning of the distillation, and condenses in yellow drops which slowly solidify to a mass resembling unbleached beeswax; at a later stage of the process the tetroxide passes over pure.

*Osmites.**—$OsMO^2$ or $M^2O.OsO^3$.—These are salts obtained by the action of reducing agents on osmic tetroxide in presence of alkalis.

*Osmite of potassium*, $OsKO^2.H^2O$, is obtained as a rose-coloured crystalline powder on adding a few drops of alcohol to a solution of the tetroxide in caustic potash (osmate of potassium) or in octahedral crystals of considerable size, by mixing the same solution with nitrite of potassium and leaving it to evaporate slowly. It may also be formed by dissolving osmic oxide in the alkaline solution of the tetroxide. It is soluble in *water*, insoluble in *alcohol* and *ether*, permanent in dry air, but changes into osmate under the influence of air and water. *Chlorine* converts it into osmic oxide and osmate of potassium. It is decomposed by *acids*, even by the weakest, osmic oxide being precipitated and osmic tetroxide evolved. *Sulphurous acid* introduced into a solution of this salt, previously rendered alkaline, throws down a yellow crystalline precipitate, containing a salt whose acid is formed of osmium, oxygen, and sulphur. *Chloride of ammonium* decomposes osmite of potassium, forming a nearly insoluble yellow salt, $2NH^4Cl.OsO^2N^2H^4$. This compound, heated in a stream of hydrogen, gives off ammonia and sal-ammoniac; and leaves metallic osmium.

*Osmite of sodium* is prepared in the same manner as osmite of potassium, but does not crystallise so easily; its solutions are rose-coloured. *Osmite of ammonium* does not appear to exist; the osmites of potassium and sodium are rapidly reduced by ammonia.

**Tetroxide of Osmium,** commonly called *Osmic acid*. $OsO^4$.—This is the volatile strong-smelling compound produced when osmium or either of its brown oxides is heated in the air or treated with nitric or nitro-muriatic acid. The best mode of obtaining it pure, according to Claus, is to rectify the distillate obtained by treating finely divided osmiridium with nitro-muriatic acid, using good means of condensation, saturate the first third of the new distillate with potash, and distil a third time. Pure tetroxide of osmium then collects in the receiver, partly in concentrated solution, partly in large beautiful crystals. Its vapour has an intolerably pungent odour, attacks the eyes strongly and painfully, and is excessively poisonous. As an antidote to its poisonous action Claus recommends the inhalation of sulphydric acid gas. Its taste is acrid and burning, but not acid. It softens like wax by the heat of the hand, melts to a colourless liquid considerably below 100°, and boils at a temperature a little above its melting point. It is dissolved slowly but in considerable quantity by *water;* the solution has no acid reaction. It is dissolved also in *alcohol* and *ether*, but the solutions are apt to decompose spontaneously, depositing metallic osmium. It is a powerful oxidising agent, decolorising *indigo-solution*, separating iodine from *iodide of potassium*, converting *alcohol* into aldehyde and acetic acid, and the *carbohydrates* into oxalic and carbonic acids. *Ammonia* decomposes it in the manner shown by the equation:

$$3OsO^4 \quad + \quad 4NH^3 \quad = \quad 3OsO^2 \quad + \quad N^4 \quad + \quad 6H^2O.$$

If the ammonia is in excess, it forms a base with the osmic oxide thus produced:

$$3OsO^4 \quad + \quad 10NH^3 \quad = \quad 3N^2H^6OsO^2 \quad + \quad N^4 \quad + \quad 6H^2O.$$

If potash is likewise present, osmiamate of potassium is formed:

$$6OsO^4 \quad + \quad 8NH^3 \quad + \quad 6KHO \quad = \quad 3K^2N^2Os^2O^5 \quad + \quad N^2 \quad + \quad 15H^2O.$$

Osmic tetroxide dissolves in *alkalis*, forming yellow or red solutions, which are inodorous in the cold, but when evaporated by heat, give off the tetroxide and leave solid residues, regarded by Berzelius, who however did not analyse them, as osmates (*i. e.* compounds of the tetroxide with alkaline oxides). But, according to Claus, a solution of the tetroxide in strong caustic potash, gives off when heated the greater part of the tetroxide, while the remainder is resolved into free oxygen and osmite of potassium, $OsKO^2$ or $K^2O.OsO^3$. A moderately strong aqueous solution of osmic tetroxide poured upon solid hydrate of potassium, becomes heated and forms, without evolution of oxygen, a blood-red solution containing nothing but osmite of potassium. (Claus.)

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* Claus designates these salts as *osmates*, because the salts so called by Berzelius do not appear to exist in definite form, the solutions of tetroxide of osmium in alkalis being always decomposed by evaporation. But it is scarcely worth while to alter the ordinary nomenclature, especially as the osmates (salts of the tetroxide) may be supposed to exist in solution.

**OSMIUM, SULPHIDES OF.** Osmium burns in sulphur-vapour. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with sulphydric acid, and the tetrasulphide by passing sulphydric acid gas into a solution of the tetroxide. It is a sulphur-acid perfectly soluble in water, whereas the others are sulphur-bases, slightly soluble in water, and forming deep yellow solutions (Berzelius). According to Claus (Jahresb. 1859, p. 264), a pure solution of osmic tetroxide yields with sulphuric acid a precipitate containing less sulphur than the tetrasulphide, $OsO^4$; but the latter may be obtained pure by previously acidulating the solution of the tetroxide with hydrochloric acid, which does not reduce it.

**OSMIUM-BASES, AMMONIACAL.** *a. Osmio-hexhydric dioxi-dinitride.* $N^2H^6OsO^2 = \left.\begin{matrix}OsN^2\\H^6O^2\end{matrix}\right\}$.—This substance is obtained in combination with 1 at. water ($N^2H^8OsO^3 = N^2H^6OsO^2.H^2O$), by the action of ammonia in excess on ammonio- or potassio-osmic chloride, or more easily by heating an aqueous solution of the tetroxide with ammonia (p. 246). It is a brown-black tasteless powder, which decomposes with scintillation when heated, dissolves in potash, less easily in ammonia, and slowly in acids. The potash-solution when heated gives off ammonia and deposits (ammoniacal) osmic hydrate. The acid solutions are red-brown, leave when evaporated uncrystallisable basic salts, only partially soluble in water, and yield with potash or ammonia a precipitate of the unaltered base. The *chloride* which remains on evaporating the solution of the base in hydrochloric acid, is a brown-black brittle mass only partially soluble in water and probably consisting of $N^2H^6OsCl^2.xH^2O$. (Claus, Jahresb. 1863, p. 303.)

*β.* Frémy (Ann. Ch. Phys. [3] xii. 221), by adding a cold solution of potassic osmite to a solution of sal-ammoniac, obtained a yellow crystalline precipitate containing, according to his analysis, $N^4H^{12}OsO^2Cl^2$, and regarded by him as a compound of sal-ammoniac with osmiamide, $2NH^4Cl, N^2H^4OsO^2$. According to Gibbs and Genth (Sill. Am. J. [2] xxv. 248), it forms a double salt with platinic chloride, and when treated with various silver-salts, yields corresponding oxy-salts which are orange-yellow, nearly insoluble in cold water, more soluble in hot water, forming solutions which are easily decomposed, with evolution of osmic tetroxide. According to Claus, Frémy's compound probably consists of $N^2H^6OsCl.H^2O$, inasmuch as it closely resembles the ruthenium-compound of analogous composition (see RUTHENIUM). The corresponding sulphate treated with baryta-water yields a very unstable solution of a base which Claus supposes to contain osmious oxide.

**OSMOSE.** See LIQUIDS, OSMOSE OF (iii. 718).

**OSSEIN.** Syn. with BONE-CARTILAGE (i. 619).

**OSTEOLITE.** A tricalcic phosphate, $Ca^3P^2O^8$, found near Hanau, also at Amberg in the Erzgebirge. A specimen from the latter locality analysed by Gorup-Besanez (Ann. Ch. Pharm. lxxxix. 221) gave 42·00 per cent. phosphoric anhydride, 48·16 lime, 4·97 silica, 1·56 ferric oxide, 0·75 magnesia, 0·04 potash, 0·02 soda, 2·21 carbonic anhydride, and 1·31 water ( = 101·02). It is probably an apatite which has lost its fluorine and chlorine. It has a compact texture, like lithographic stone, or else is earthy and adheres to the tongue. Specific gravity = 2·89. (Bromeis, Ann. Ch. Pharm. lxxix. 1.)

**OSTRANITE.** A greyish-brown zircon from Brevig in Norway.

**OSTREOCOLLA.** A name of earthy limestone.

**OTHYL** (contraction of *Ox-ethyl*). The name given by Williamson to the acid radicle $C^2H^3O$, commonly called *acetyl*. (See NOMENCLATURE, p. 132.)

**OTOBA-FAT.** Obtained from the fruit of *Myristica otoba*. It is nearly colourless, buttery, smells like nutmegs when fresh, disagreeably in the melted state. Melts at 35°. Contains myristin, olein, and otobite. (Uricoechea, Ann. Ch. Pharm. xci. 369.)

*Otobite.*—When otoba-fat is saponified and the soap is treated with alcoholic acetate of magnesium, a precipitate is formed containing otobite and myristic acid; and on dissolving out the latter with alcohol, the otobite remains and may be purified by recrystallisation from hot alcohol or ether. It forms large colourless prisms having a glassy lustre, tasteless and inodorous, melting at 133°, and solidifying in the crystalline, or if more strongly heated, in the amorphous state. It is not volatile, but creeps up the sides of the tube when heated. Contains on the average 73·02 C, 6·40 H, and 20·58 O, agreeing nearly with the formula $C^{24}H^{26}O^5$. (Uricoechea.)

**OTTRELITE.** A silicate of micaceous structure occurring at Ottrez, near Stavelot, on the borders of Belgium and Luxembourg, in small shining scales or plates disseminated through the gangue. Specific gravity = 4·4. Scratches glass with difficulty, has a blackish, greenish-grey or black colour, and pale green streak. Before the blowpipe it fuses with difficulty to a black magnetic globule, and gives with fluxes the reactions of iron and manganese. Contains 43·34 per cent. silica, 24·63 alumina, 16·72 ferrous oxide, 8·18 manganous oxide, and 5·66 water ( = 98·68) agreeing approximately with the formula $3(Fe\,;\,Mn)''SiO^3.\overline{\overline{Al}}{}^4Si^3O^{12}$.

*Phyllite* (*q. v.*) from Sterling, Massachusetts, is regarded by Dana as identical with ottrelite, but the analyses of the two minerals differ considerably.

**OUVAROVITE.** Lime-chrome garnet from Bisserak in the Ural. (See GARNET, ii. 772.)

**OWALA** or *Opochala*. A leguminous plant growing on the Gaboon and near Fernando Po, the seeds of which yield a fat oil. (Arnaudon, J. Pharm. [3] xxxvii. 404.)

**OWENITE.** Thuringite from the Potomac. (See THURINGITE.)

**OXABENZIDIDE.** $C^{14}H^{10}N^2O^2 = N^2\left\{\begin{matrix}(C^{12}H^8)''\\(C^2O^2)''\\H^2\end{matrix}\right.$.—A substance obtained by heating oxalate of benzidine, $C^{12}H^{12}N^2.C^2H^2O^4 - 2H^2O = C^{14}H^{10}N^2O^2$. It is pulverulent, quite insoluble in water, alcohol, ether, dilute acids, and alkalis, and is resolved by strong potash into oxalic acid and benzidine. (Borodine, Zeitschr. Ch. Pharm. 1860, p. 533.)

**OXACALCITE.** Native oxalate of calcium (p. 255).

**OXACETIC ACID.** Syn. with GLYCOLLIC ACID.

**OXALACETIC ACID.** A name applied by Dumas and Piria (Ann. Ch. Phys. [3] v. 353) to tartaric acid, from a peculiar view which they held of its constitution.

**OXALAN.** Syn. with OXALURAMIDE (*q. v.*).

**OXALANTIN.** $C^6H^4N^4O^5$. (Limpricht, Ann. Ch. Pharm. cxi. 133.)—A body produced by the action of nascent hydrogen on parabanic acid:

$$\underset{\text{Parabanic acid.}}{2C^3H^2N^2O^3} + H^2 = \underset{\text{Oxalantin.}}{C^6H^4N^4O^5.H^2O};$$

it is related to parabanic acid in the same manner as alloxantin $C^8H^4N^4O^7$, to alloxan $C^4H^2N^2O^4$.

It is obtained in the form of a zinc-compound by the action of zinc and hydrochloric acid on parabanic acid; on treating the crystalline powder thus produced with sulphydric acid, and evaporating the filtrate, oxalantin is obtained in hard white crusts, having when dried at 100°, the composition $C^6H^4N^4O^5.H^2O$. It is sparingly soluble in water, nearly insoluble in alcohol and ether; the aqueous solution has a slight acid reaction. It is not oxidised by nitric acid or peroxide of lead at the boiling heat, but when its aqueous solution is heated with mercuric oxide or silver-nitrate and ammonia is added, reduction takes place immediately. Oxalantin dissolves easily in alkalis and alkaline carbonates, with effervescence in the latter case. The solutions when evaporated appear to contain oxaluric acid.

**OXALIC ACID.** $C^2H^2O^4 = \left.\begin{matrix}(C^2O^2)''\\H^2\end{matrix}\right\}O^2$. *Oxalsäure. Kleesäure. Sauerkleesäure. Kohlige Säure. Acide oxalique. Acide carboneux.*—This acid, the first of the series of dibasic acids, $C^nH^{2n-2}O^4$, including malonic, succinic, pimelic acid, &c. (i. 52), was first obtained by Savary in 1773, and Wiegler in 1779, in the form of a sublimate and an aqueous distillate, by heating salt of sorrel. Scheele first prepared it from salt of sorrel by means of basic acetate of lead, and showed that the acid thus obtained was identical with the *acid of sugar* previously prepared from sugar and nitric acid, and investigated by Bergman. Its composition was established by Dulong, Döbereiner, and Berzelius. (For the literature relating to it, see *Gmelin's Handbook*, ix. 111.)

*Occurrence.*—Oxalic acid occurs very frequently in living plants; as a potassium-salt in various species of *Rumex* and *Oxalis*; as a sodium-salt in most species of *Salsola* and *Salicornia*, plants growing in salt-marshes; as a calcium-salt in a great number of plants, in the root, bark, leaves, &c., being often found in the cells in the form of small crystals, the so-called *raphides*. Many lichens are very rich in oxalate of calcium. Ferrous oxalate occurs in deposits of lignite. The free acid (hydric oxalate) is found in *Boletus igniarius*, and, according to some statements, in the juice of the chick-pea. Oxalate of calcium is also of frequent occurrence in the animal body, being found in urine, urinary deposits, and calculi; in the allantoic liquid of the cow; in the mucus of the gall-bladder of men, oxen, dogs, rabbits, and pikes; and in the Malpighian vessels of the caterpillar of *Sphinx Convolvuli*.

*Formation.*—1. Oxalic acid is a very frequent product of the oxidation of other organic compounds, being in fact the most highly oxidised of all carbon-compounds except carbonic anhydride. Some compounds, namely alcohol $C^2H^6O$, glycol $C^2H^6O^2$, and glycollic acid $C^2H^4O^3$, are converted into oxalic acid by a comparatively simple process of oxidation; but in most cases the reaction is more complex, resulting in a complete breaking up of the molecule. In this manner oxalic acid is produced in great abundance from the more highly carbonised organic substances, such as the carbohydrates, sugar, starch, cellulose, &c.; α. by the action of nitric acid; β. by fusion with caustic alkalis. It is also produced in considerable quantity by the action of moist chlorine or chlorine-water on uric acid.—2. As an ammonium-salt, together with other products, in the decomposition of cyanogen by water:

$$C^2N^2 \quad + \quad 4H^2O \quad = \quad C^2(NH^4)^2O^4.$$

3. As a potassium-salt by heating potassic formate with excess of potassic hydrate, the action being attended with evolution of hydrogen:

$$2CHKO^2 \quad = \quad C^2K^2O^4 \quad + \quad H^2.$$

4. It is also found among the secondary products obtained in the preparation of potassium by heating potassic carbonate with charcoal.

*Preparation.*—1. From *Acid Oxalate of Potassium* (salt of sorrel) by precipitating the solution of the salt with acetate of lead, and decomposing the precipitated oxalate of lead with sulphuric or sulphydric acid. This is the oldest mode of preparation, but it has given place to the following more productive methods.

2. *From Sugar.*—1 pt. of loaf-sugar is heated with 8 pts. of nitric acid of specific gravity 1·38 ultimately to the boiling point, and the solution is evaporated down to one-sixth; it then on cooling deposits white crystals of oxalic acid. It is important in this process to use a sufficient quantity of nitric acid, as the mother-liquor then crystallises in the form of oxalic acid, down to the last drop; but if less nitric acid has been added, saccharic acid and other intermediate products remain in the mother-liquor, which then becomes yellow and brown on evaporation. The crystals of oxalic acid may be purified from adhering mother-liquor by recrystallising them from water containing a little nitric acid, then draining them on a funnel, washing with a little cold water, and drying between bibulous paper at a medium temperature. Oxalic acid prepared with nitric acid is often contaminated with the latter, which may however be removed by allowing the crystals to effloresce in warm air, then recrystallising from hot water, again leaving them to effloresce, and recrystallising. (Berzelius.)

Moist sugar, treacle, starch-sugar or starch may also be used instead of loaf-sugar for the preparation of oxalic acid. The nitrous fumes evolved in the process may be utilised for the manufacture of sulphuric acid; or they may be reconverted into nitric acid by the action of air and water. (For a description of the manufacture of oxalic acid on the large scale, and of several patented processes for utilising the nitrous fumes, see *Ure's Dictionary of Arts, &c.* iv. 367. also *Richardson and Watts's Chemical Technology*, vol. i. pt. 5.)

3. *From Starch, Cellulose and other Organic substances by fusion with alkaline hydrates.*—When 100 pts. of starch, sawdust, straw, hay, bran, tobacco-cuttings, &c., is mixed with a solution of about 300 pts. hydrate of potassium, the liquid evaporated, and the residue heated to 200°—250° for four or five hours, a quantity of oxalic acid is obtained amounting to between 100 and 150 pts. of the crystallised acid. When soda is used instead of potash, the product is much less; but with a mixture of 1 pt. hydrate of sodium to 2 pts. hydrate of potassium, it is somewhat greater than with potash alone (Possoz, Compt. rend. xlvii. 207, 648). A process founded on this reaction has been patented by Messrs. Roberts Dale and Pritchard of Manchester, who prepare oxalic acid on a considerable scale by heating sawdust with a mixture of potassic and sodic hydrates. On treating the product with a small quantity of water, sodic oxalate alone remains undissolved. This salt is converted into calcic oxalate by treatment with chloride of calcium; the calcic oxalate is decomposed by dilute sulphuric acid; and the oxalic acid is left to crystallise from the filtrate by cooling. (*Chemical Technology*, loc. cit.)

*Properties.*—Oxalic acid crystallises easily in large transparent colourless crystals, containing 2 at. water: $C^2H^2O^4.2H^2O$. They belong to the monoclinic system, usually exhibiting the combination $\infty P . oP . + P\infty . - P\infty . [P\infty]$. Ratio of axes, $a : b : c = 0·590 : 1 : 1·969$. Angle $b : c = 73° 48'$; $\infty P : \infty P = 116° 52'$; $\infty P : + P\infty = 117° 2'$; $- P\infty : oP = 129° 20'$; $- P\infty : + P\infty = 127° 16'$; $+ P\infty : oP = 103° 24'$; $\infty P : [P\infty] = 140° 19'$. The crystals are usually prismatically elongated in the direction of the orthodiagonal. (Brooke, Ann. Phil. xxii. 19.—De la Provostaye, Ann. Ch. Phys. [3] iv. 453.—Rammelsberg, Pogg. Ann. xciii. 24.)

Oxalic acid is very soluble in *water* and in *alcohol*, dissolving in 15·5 pts. water at 10°, in 9·5 pts. at 13·9° and in a very small quantity at 100° (Turner). The solution is strongly acid and very poisonous, reddens litmus, and decomposes carbonates with effervescence. Oxalic acid contaminated with nitric acid dissolves in 2 pts. of cold water (Berzelius). (See further Storer's *Dictionary of Solubilities*, p. 419.)

Crystallised oxalic acid melts at about 98° in its water of crystallisation; on continued heating, part of it sublimes as dry oxalic acid, $C^2H^2O^4$, while the greater part suffers decomposition. It also gradually gives off its water over oil of vitriol at 20°, being completely dehydrated in the course of a few weeks (Erdmann, J. pr. Chem. lxxxv. 213). According to Bödeker (Jahresb. 1860, p. 17), the specific gravity of the crystallised acid is 1·63; of the sublimed acid 2·0. The acid dried at 100° sublimes at 165° in slender white needles, part of it however being decomposed, and in greater proportion as the temperature is higher.

*Decompositions.*—1. Oxalic acid is resolved by *heat* into carbonic anhydride and formic acid, part of the latter being further resolved into carbonic oxide and water:

$$C^2H^2O^4 = CO^2 + CH^2O^2$$
$$C^2H^2O^4 = CO^2 + CO + H^2O.$$

The same decomposition takes place when the acid is heated with *platinum-sponge*, *pumice* or *sand*. When oxalic acid is heated with an equal weight of *glycerin*, decomposition takes place at about 100°, carbonic anhydride being evolved, and the residue, probably a compound of formic acid with glycerin, yields formic acid by distillation with water (ii. 686).

2. Oxalic acid heated with *dehydrating substances*, such as concentrated *sulphuric* or *phosphoric acid*, is resolved into water and equal volumes of carbonic oxide and carbonic anhydride:

$$C^2H^2O^4 = H^2O + CO + CO^2.$$

3. An analogous decomposition is produced by *pentachloride of phosphorus*, the products being carbonic oxide, carbonic anhydride, hydrochloric acid and oxychloride of phosphorus:

$$C^2H^2O^4 + PCl^5 = CO + CO^2 + 2HCl + POCl^3.$$

As this and the preceding reaction, when applied to other dibasic acids, yield the corresponding anhydrides (i. 52), and as moreover the reaction with pentachloride of phosphorus takes place in exactly the same manner when the two bodies are brought together in strongly cooled ether or sulphide of carbon (Kekulé), it appears probable that the anhydride of oxalic acid, $C^2O^3$, is unable to exist under any conditions that we are able to command.

4. *Trichloride of phosphorus* acts on the dry acid in the same manner as the pentachloride; with crystallised oxalic acid, however, it yields crystallisable phosphorous acid (Hurtzig and Geuther, Ann. Ch. Pharm. cxi. 170):

$$C^2H^2O^4.2H^2O + PCl^3 = CO + CO^2 + 3HCl + PH^3O^3.$$

5. Oxalic acid is not readily attacked by *nitric acid;* it may indeed be crystallised from hot nitric acid; by continued boiling therewith however it is slowly oxidised, yielding water and carbonic anhydride.

6. By other *oxidising agents*, oxalic acid is easily resolved into carbonic anhydride and water. Thus it is oxidised slowly by the *oxygen of the air* in presence of platinum black; quickly by *peroxide of lead* or *peroxide of manganese* in presence of an acid: *e. g.*

$$C^2H^2O^4 + MnO^2 + H^2SO^4 = 2CO^2 + 2H^2O + MnSO^4.$$

On this reaction is founded a convenient method of valuation of commercial oxide of manganese (iii. 814). When these peroxides act on aqueous oxalic acid, the products are carbonic anhydride and a metallic oxalate, *e. g.*

$$2C^2H^2O^4 + MnO = 2CO^2 + H^2O + C^2MnO^4.$$

When 4 pts. of dried oxalic acid are triturated with 21 pts. peroxide of lead, the mass becomes incandescent. Oxalic acid is likewise rapidly oxidised by *potassic permanganate*, *chromic acid* and *vanadic acid*.

7. *Chlorine* does not act on dry oxalic acid; but in presence of water, decomposition quickly takes place, thus:

$$C^2H^2O^4 + Cl^2 = 2CO^2 + 2HCl.$$

A similar reaction is produced by *bromine*, *hypochlorous acid*, and the *chlorides of easily* *reducible metals.* Hence oxalic acid precipitates metallic gold from *auric chloride*, especially on boiling; also metallic platinum from *platinic chloride*, but only under the influence of direct sunshine. With *mercuric chloride*, oxalate of ammonium quickly forms mercurous chloride.

8. *Potassium and sodium* heated with dry oxalic acid, decompose it with incandescence, charcoal being separated and hydrogen evolved.

9. When oxalic acid is heated with excess of *potassic* or *barytic hydrate*, hydrogen is evolved and a carbonate is formed: *e.g.*

$$C^2H^2O^4 \quad + \quad 2KHO \quad = \quad 2KHCO^3 \quad + \quad H^2.$$

10. *Nascent hydrogen*, evolved by the action of sodium-amalgam on water, or of zinc on dilute sulphuric acid, converts oxalic into glyoxylic acid: $C^2H^2O^4 + H^2 = C^2H^2O^3.H^2O$. (Church, ii. 922.)

**Oxalates.** Oxalic acid is dibasic, yielding with monatomic metals, neutral salts containing $C^2M^2O^4$, and acid salts $C^2HMO^4$. With potassium and ammonium it likewise forms hyper-acid salts, *e. g.* $C^2HKO^4.C^2H^2O^4$, or $C^4H^3KO^8$. With most diatomic metals it forms only one salt; with barium and strontium, however, it forms acid salts analogous to the hyperacid oxalates of the alkali-metals. It also forms numerous well-crystallised double salts. It is one of the strongest acids, decomposing dry chloride of sodium when heated, with evolution of hydrochloric acid, and converting chloride or nitrate of sodium in aqueous solution into acid oxalate.

The oxalates of the alkali-metals are soluble in *water*, the rest are for the most part insoluble in water, but soluble in dilute *acids*.

All oxalates are decomposed by *heat*. The oxalates of the alkali-metals, and also of the alkaline earth-metals, if not too strongly heated, give off carbonic oxide, and leave carbonates, while the oxalates of those metals whose carbonates are decomposed by heat (zinc and magnesium for example) give off carbonic oxide and carbonic anhydride and leave metallic oxides. The oxalates of the more easily reducible metals (silver, copper, &c.) give off carbonic anhydride and leave the metal; the lead-salt leaves suboxide of lead, and gives off 3 vol. carbonic anhydride to 1 vol. carbonic oxide:

$$2C^2Pb''O^4 \quad = \quad Pb^2O + 3CO^2 + CO.$$

Oxalates heated with *sulphuric acid* give off carbonic oxide and carbonic anhydride, and leave a residue of sulphate. In this case, as well as in the decomposition by heat alone, no separation of carbon takes place, and consequently the residue does not blacken; this character distinguishes the oxalates from the salts of all other carbon-acids.

Oxalic acid and the soluble oxalates give with *chloride of calcium* a precipitate of calcic oxalate, insoluble in water and in acetic acid, but soluble in hydrochloric and nitric acid. This reaction affords a very delicate test for the presence of oxalic acid: the insolubility of the precipitated oxalate in acetic acid distinguishes it at once from the phosphate.

Precipitation with soluble calcium-salts serves also for the quantitative estimation of oxalic acid, the precipitate being converted at a low red heat into carbonate $C^2Ca''O^3$, 100 pts. of which are equivalent to 128 pts. calcic oxalate $C^2Ca''O^4$, 90 pts. dry oxalic acid $C^2H^2O^4$, or 126 pts. of the crystallised acid $C^2H^2O^4.2H^2O$. The carbon and hydrogen in oxalates may also be estimated by combustion with oxide of copper.

The composition and properties of the oxalates have been made the subject of numerous researches, especially by Berzelius, and more recently by Rammelsberg (Pogg. Ann. xciii. 24) and Souchay and Lenssen (Ann. Ch. Pharm. xcix. 31; c. 308; cii. 35 and 41; ciii. 308; cv. 245; Jahresb. 1856, 446; 1857, p. 289; 1858, p. 243).

OXALATE OF ALUMINIUM.—A solution of alumina in oxalic acid leaves on evaporation an amorphous transparent mass, which has a sweetish astringent taste, reddens litmus, deliquesces in the air, and swells up when heated.

*Sodio-aluminic Oxalate*, $\overset{vi}{Al}{}^2O^3.2Na^2O.4C^2O^3.10H^2O$ or $\left.\begin{matrix}(\overset{''}{C}{}^2O^2)^4\\ \overset{vi}{Al}{}^2.Na^4\end{matrix}\right\}O^8.10H^2O$, is produced when an excess of basic sulphate of aluminium (obtained by precipitating alum with excess of sodic carbonate) is boiled for a long time with a solution containing 1 at. sodic carbonate to 3 at. oxalic acid. The liquid if left to itself, for some months deposits the double salt in rhombic crystals, permanent in the air, and sparingly soluble in water with separation of alumina or basic salt. (Lenssen and Löwenthal, J. pr. Chem. lxxxvi. 314.)

OXALATES OF AMMONIUM.—*a. Neutral salt*, $C^2(NH^4)^2O^4.H^2O$.—This salt has been found in guano. It is obtained by saturating oxalic acid with ammonia or its carbonate, and crystallises in colourless rhombic prisms generally exhibiting the combination ∞P . oP . ∞P̆∞ 2P̆∞ . ½P. Ratio of axes, $a : b : c = 0{\cdot}7837 : 1 : 0{\cdot}3711$. Angle ∞P : ∞P = 76° 10′; ∞P : ∞P̆∞ = 128° 5′; oP : ½P = 148° 55′; 2P̆∞ : oP = 143° 26′; 2P̆∞ : ½P = 151°30′. The crystals are partly hemihedral, only two of the four faces ½P being present at each end. One of the faces ½P∞ and the adjacent face 2P∞ are usually of larger dimensions than the posterior faces at the same end; moreover the crystals are often flattened, two of the prismatic faces ∞P then disappearing (De la Provostaye, Ann. Ch. Phys. [3] iv. 454.—Brooke, Ann. Phil. xxii. 374). The crystals effloresce in warm air, giving off 1 at. water. They dissolve in 3 pts. of cold water, but according to Heintz (J. pr. Chem. lxxxvii. 309) are much less soluble in water containing ammoniacal salts, so that the salt is precipitated from a moderately strong solution on addition of chloride or acetate of ammonium. The salt is decomposed by dry distillation, yielding oxamide and other products.

*β. Acid Oxalate, Di-oxalate*, or *Bi-oxalate*, $C^2H(NH^4)O^4.H^2O$.—Produced by mixing the solution of the neutral-salt with oxalic acid, or with any other acid, such as sulphuric, hydrochloric, or nitric. It crystallises in rhombic prisms, usually exhibiting the combination ∞P : P̄∞ . P̆2 . P̄∞, with the terminal faces oP, ∞P̆∞ and ∞P̄∞. Ratio of axes, $a : b : c = 0{\cdot}4533 : 1 : 0{\cdot}5593$. Angle ∞P : ∞P̆∞ = 114° 23′; P̆∞ : oP = 150° 47′; ∞P̄∞ : ∞P = 155° 37′; oP : ∞P̆∞ = 90°; oP : ∞P̄∞ = 90°; P̆∞ : ∞P̆∞ = 119° 13′; oP : P̄∞ = 129° 1′; P̆2 : P̄∞ = 151° 42′; P̆2 : oP = 140° 13′. This salt has an acid reaction, and is less soluble in water than the neutral oxalate. It is resolved by heat into oxamide and oxamic acid.

*Hyperacid Oxalate, Tetroxalate* or *Quadroxalate*, $C^2H(NH^4)O^4.C^2H^2O^4.2H^2O$ or $C^4H^3(NH^4)O^8.H^2O$.—Obtained by crystallising a mixture of equal parts of the preceding salt and oxalic acid. It crystallises in triclinic prisms isomorphous with the hyperacid potassium-salt, and having a specific gravity of 1·607 (Schiff). The crystals effloresce at 100°, giving off 15·4 per cent. = 2 at. water. They are very soluble in warm water.

OXALATE OF ANTIMONY, $\overset{'''}{Sb}{}^2O^3.C^4O^6.2H^2O$ or $2[C^6Sb'''H^3O^{12}.\overset{'''}{Sb}{}^2O^3].3H^2O$ =

$2\left[\left.\begin{matrix}(\overset{''}{C^2O^2})^3\\ \overset{'''}{Sb}{}^2H^3\end{matrix}\right\}O^6\right]\cdot 3H^2O$.—This salt is prepared by boiling antimonious chloride or the oxychloride (algaroth-powder) with oxalic acid (Péligot), or by mixing a saturated aqueous solution of oxalic acid with a solution of trichloride of antimony in hydrochloric acid (Souchay and Lenssen); it then separates in the course of 24 hours as a granular precipitate. It gives off 1 at. water at 100° and begins to decompose at 220°. (Souchay and Lenssen.)

*Ammonio-antimonic Oxalate.* $C^6Sb'''(NH^4)^3O^{12}.2H^2O$.—Obtained by mixing a solution of antimonious oxide in acid oxalate of ammonium, first with a small quantity of absolute alcohol (which throws down acid oxalate of ammonium), then, after filtering, with about three times its volume of absolute alcohol (Souchay and Lenssen). It forms rhombic prisms exhibiting the combination oP . P . 2P . ∞P̆∞. Axes $a : b : c = 0{\cdot}3716 : 1 : 0{\cdot}5305$. (Rammelsberg.)

*Potassio-antimonic Oxalate.* $C^6Sb'''K^3O^{12}.6H^2O$.—Obtained by dissolving antimonious oxide in a hot concentrated solution of acid oxalate of potassium. The filtrate, as it cools, deposits nodular crystals of the salt, which dissolve without decomposition in water, but are decomposed by mineral acids, with separation of oxalic acid or of basic oxalate of antimony. Gives off 3 at. water at 100° (Souchay and Lenssen). According to Rammelsberg, the salt prepared as above forms monoclinic crystals containing $2C^6Sb'''K^3O^{12}.3H^2O$. Ordinary combination ∞P . ∞P∞ . oP . [∞P∞]. Ratio of axes, $a : b : c : = 1{\cdot}2364 : 1 : 0{\cdot}5472$. Angle of inclined axes = 69° 36; ∞P : ∞P in the clinodiagonal principal section = 105° 40′; [P∞] : [P∞], in the same = 134° 56′; oP : ∞P = 106° 8′ (Rammelsberg). On dissolving this salt in water, part of it decomposes, with separation of oxide of antimony, while the rest dissolves without alteration, and separates after awhile in large crystals containing $2C^6Sb'''K^3O^{12}.9H^2O$. These crystals are rhombic, generally exhibiting the combination ∞P . P̆∞ . P̄∞ . ∞P̆∞. Ratio of axes, $a : b : c = 0{\cdot}6903 : 1 : 1{\cdot}14163$. Angle ∞P : ∞P = 67° 40′; P̆∞ : P̆∞ (basal) = 97° 48′; P̄∞ : P̄∞ (basal) = 119° 23′. The mother-liquor of this salt deposits, besides acid and hyperacid oxalate of potassium, a few crystals of a double salt belonging to the triclinic system. (Rammelsberg.)

*Sodio-antimonic Oxalate.* $C^6Sb'''Na^3O^{12}.C^2Na^2O^4.10H^2O$.—Prepared like the potassium-salt. Forms distinct highly lustrous crystals, which give off half their water when heated for some time to 100°. Dissolves without decomposition in water either hot or cold, but is decomposed by mineral acids. Sparingly soluble in alcohol, insoluble in ether. (Souchay and Lenssen.)

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**OXALATES OF ARSENIC.** *Potassio-arsenious oxalate*, $C^6As'''K^3O^{12}.3H^2O$?—Deposited in small hard glassy crystals from a hot solution of arsenious oxide in aqueous acid oxalate of potassium. (Souchay and Lenssen.)

**OXALATES OF BARIUM.** The *neutral* salt, $C^4Ba''O^8.2H^2O$, is precipitated as a white powder on mixing oxalic acid with excess of baryta-water, or by precipitating the neutral potassium-salt with chloride of barium. It dissolves in 2,590 pts. of cold, and 2,500 pts. of hot water, more readily in solution of sal-ammoniac, still more in water containing acetic acid, and most readily in aqueous oxalic acid. At 100° it gives off 1 at. water, and is reduced to $C^4Ba''O^8.H^2O$, which is also the composition of the salt obtained by precipitating a solution of chloride of barium with oxalate of ammonia, at the boiling heat.

An *acid oxalate*, $C^4H^2Ba''O^4.4H^2O$, is deposited in pointed crystals on mixing nearly equal quantities of the saturated solutions of oxalic acid and chloride of barium. The crystals dissolve in 336 pts. of water at 15·5°, forming an acid solution; they are decomposed by hot water, converted into the normal oxalate by saline solutions, and are not altered by alcohol or ether (Clapton, Chem. Soc. Qu. J. v. 223). According to Souchay and Lenssen, they contain only half the water required by the formula above given, half of this water going off at 100°, the rest at 145°, and oxalic acid beginning to volatilise at the same time. The crystals require 392 pts. of water at 17° to dissolve them, and are decomposed by hot water, with formation of the neutral salt; alcohol likewise throws down the neutral salt from the aqueous solution of the acid salt.

**OXALATES OF BISMUTH.** $C^6\overset{'''}{Bi}{}^2O^{12}.15H^2O$.—The *neutral-salt* separates as a white crystalline precipitate on mixing nitrate of bismuth with excess of oxalic acid. Retains 2 at. water at 100°, but decomposes at higher temperatures into suboxide of bismuth ($Bi^2O^2$) and acid oxalate of bismuth. It is insoluble in water, soluble in acids, and decomposes by prolonged contact with water into oxalic acid which dissolves and a basic oxalate of bismuth. (Souchay and Lenssen.)

*Basic oxalate.* The neutral oxalate boiled with water yields a salt having the composition $2(Bi^2O^3.C^4O^6).3H^2O$ (Heintz). Souchay and Lenssen, by boiling the recently precipitated normal oxalate with water till the liquid no longer became acid, obtained a salt which gave by analysis 72·39 per cent. oxide, agreeing with the formula $Bi^2O^3.C^4O^6.2H^2O$ or $2(C^6Bi'''H^3O^{12}.\overset{'''}{Bi}{}^2O^3).3H^2O$ (requiring 72·05 per cent. $BiO^3$) better than with Heintz's formula, which requires 73·5 per cent. According to the latter formula the salt is analogous to the oxalate of antimony above described.

*Oxalate of Bismuth and Ammonium.* $C^6Bi'''(NH^4)^3O^{12}.6C^2(NH^4)^2O^4.12H^2O$.—Crystallises from a hot saturated solution of oxalate of bismuth in oxalate of ammonia, in small prismatic crystals which give off the whole of their water (13·98 per cent.) at 100°. Dissolves readily in hot water, forming a clear solution which becomes turbid after a few seconds, and deposits oxalate of bismuth as a crystalline powder. It is insoluble in alcohol and ether. (Souchay and Lenssen.)

*Oxalate of Bismuth and Potassium.* $C^6Bi'''K^3O^{12}.2C^2K^2O^4.12H^2O$.—Prepared like the preceding, and separates in small prismatic crystals which are insoluble in alcohol and ether, and are decomposed by water. The mother-liquor deposits a salt containing $C^6Bi'''K^3O^{12}.4C^2K^2O^4.12H^2O$. (Souchay and Lenssen.)

**OXALATE OF CADMIUM.** $C^2Cd''O^4.3H^2O$.—The anhydrous salt is obtained as a white amorphous powder by digesting carbonate of cadmium with oxalic acid. Oxalic acid or oxalate of ammonia added to chloride of cadmium throws down the tri-hydrated salt as a white precipitate consisting of microscopic tabular crystals, soluble in 13,000 pts. of cold and 11,000 pts. of boiling water, a little more soluble in water and oxalic acid, easily soluble in mineral acids, ammonia and ammoniacal salts. Gives off all its water at 100°, and is decomposed at 340°, leaving a mixture of cadmium-oxide and metallic cadmium. (Souchay and Lenssen.)

*Oxalate of Cadm-ammonium.* $C^2(N^2H^6Cd)''O^4.2H^2O$.—When oxalate of cadmium is added to ammonia till no more is dissolved on heating the liquid, the filtrate left for some time in the cold deposits needle-shaped crystals, which rapidly give off part of their ammonia when exposed to the air, and at 100° give off water as well as ammonia, acquiring at the same time a slight brownish tint, from separation of cadmium—oxide. (Souchay and Lenssen.)

*Ammonio-cadmic Oxalates.*—*α.* $C^4Cd''(NH^4)^2O^8.5C^2(NH^4)^2O^4.9H^2O$.—Separates in microscopic crystals when a solution of oxalate of cadmium in oxalate of ammonium saturated at the boiling heat, is diluted after filtration with an equal volume of water. Gives off all its water at 100°. (Souchay and Lenssen.)

*β.* $C^4Cd''(NH^4)^2O^8.7C^2(NH^4)^2O^4.11H^2O$.—Separates in hard crystalline crusts from the preceding saturated solution, if left to cool without addition of water. (Souchay and Lenssen.)

γ. Rammelsberg by dissolving oxide of cadmium in oxalate of ammonium, obtained a salt to which he assigned the formula $C^4Cd''(NH^4)^2O^8.3C^2(NH^4)^2O^4.8H^2O$. This salt is supposed by Souchay and Lenssen to contain only $7H^2O$. The three double-salts then form a regular series, their formulæ, if A stand for $C^4Cd''(NH^4)^2O^8$, and B for $C^2(NH^4)^2O^4$, being $A.B^4.11H^2O$, $A.B^3.9H^2O$, and $A.B^2.7H^2O$. (Souchay and Lenssen.)

*Potassio-cadmic Oxalate*, $C^4Cd''K^2O^8.2HO$, is produced by saturating a boiling solution of oxalate of potassium with oxalate of cadmium, and separates from the filtrate in microscopic square-based octahedrons, which give off their water at 100° and are decomposed by water.

*Sodio-cadmic Oxalate.* $C^4Cd''Na^2O^8.2H^2O$.—Similar to the potassium-salt. (Souchay and Lenesen.)

**Oxalate of Calcium**, $C^2Ca''O^4$.—This salt is very widely diffused in the vegetable kingdom, being found in the juice of most plants, whence it is deposited on the vascular tissue, towards the end of the growing season, in microscopic crystals having the form of a square-based octahedron (P : P in the terminal edges of the primary octahedron 46° 28′; in a more obtuse octahedron modifying the first = 119° 34′). According to Braconnot (Ann. Ch. Phys. [2] xxviii. 318), it often constitutes about half the weight of lichens growing on calcareous stones. The marble of the Parthenon at Athens is encrusted in some parts with a greyish, warty, and somewhat opaline coating of calcic oxalate about a line thick, called *Thierschite* by Liebig, which is supposed to have been deposited by lichens growing on the stone. Calcic oxalate has also been found by Schmidt (Ann. Ch. Pharm. lxi. 304) in beer-yeast. It is also of frequent occurrence in the animal body (p. 250).

Calcic oxalate is precipitated as a white powder whenever a soluble calcium-salt is mixed with oxalic acid or an alkaline oxalate, provided there be no strong mineral acid present in large excess. It is insoluble in water, acetic acid, and solution of sal-ammoniac, nearly insoluble in free oxalic acid, and sparingly soluble in lactic acid, but it dissolves with tolerable facility in hydrochloric or nitric acid, whence it is precipitated by caustic alkalis or alkaline carbonates. Chloride of magnesium also renders it slightly soluble in water. (Turner, Pogg. Ann. xix. 148.)

Oxalate of calcium is insoluble in hot concentrated solutions of the chlorides of potassium, sodium, ammonium, barium, strontium and calcium, but soluble to a considerable extent in hot solutions of salts of the metals belonging to the magnesian group, and is precipitated from these solutions by an excess of alkaline oxalate (Souchay and Lenssen). When immersed in a solution of cupric salt (*e. g.* the sulphate, chloride, or nitrate) it is gradually converted into cupric oxalate, a soluble calcium-salt being formed at the same time. In presence of a large quantity of chloride of sodium, calcium, or ammonium, oxalate of calcium dissolves completely in solution of cupric chloride; but if the solution be agitated or left to stand for some time, cupric oxalate separates out. When oxalate of calcium is boiled with a soluble salt of silver, lead, cadmium, zinc, nickel, cobalt, strontium, or barium, a soluble calcium-salt is formed, and an oxalate of the other base is precipitated. (A. Reynoso, Compt. rend. xxix. 527.)

Oxalate of calcium dissolves in considerable quantity in pure *phosphoric acid*, especially with the aid of heat. Such a solution when largely diluted with water, remains clear if it contains a large quantity of phosphoric acid; and if caustic-soda be then cautiously added till the precipitate formed at first is redissolved, and the liquid then left to stand quietly, a large proportion of the calcic oxalate crystallises within twenty-four hours in quadratic pyramids; and the mother-liquor if again treated with soda, yields another crop of crystals. (Neubauer, Ann. Ch. Pharm. xcix. 223.)

Oxalate of calcium dried at 38° contains 2 at. water ($C^2Ca''O^4.2H^2O$), half of which is given off at 100°, the rest at a higher temperature (Thomson. Graham). The salt dried at 150° is highly electric, but loses this property as it absorbs moisture from the air. (Berzelius.)

According to E. Schmid (Ann. Ch. Pharm. xcvii. 225), the precipitate of calcic oxalate obtained by mixing neutral solutions of chloride of calcium and potassic oxalate, and left to dry for a considerable time at ordinary temperatures in the air, or for a shorter time in vacuo over sulphuric acid, consists of $C^2Ca''O^4.2H^2O$ (water by analysis, 12·3 per cent.; by calculation, 12·1). The precipitate thus obtained did not exhibit distinctly angular terminations, even with a magnifying power of 300°; but that which was produced by slowly adding a solution of potassic oxalate to solution of chloride of calcium, exhibited under the microscope, dendrites and laminæ made up of oblique prismatic tables, and appeared to consist of a mixture of the hydrates $C^2Ca''O^4.2H^2O$ and $C^2Ca''O^4.H^2O$.

According to Souchay and Lenssen, oxalate of calcium, dried in the air at ordinary temperatures, contains sometimes 1 at., sometimes 3 at. water; and when dried at 100°, always 1 at., half of which is given off at 180°, and the remainder at a temperature considerably above 200°; on exposing the anhydrous salt to the air, the 1 at.

water is quickly reabsorbed. A salt with 2 at. water does not appear to exist.—Oxalate of calcium precipitated at the boiling heat from a mixture of solutions of chloride of calcium and oxalate of ammonium, contains $C^2Ca''O^4.H^2O$; so likewise when precipitated in the cold from concentrated solutions, whether neutral or alkaline; but the salt precipated in the cold from dilute solutions, is always a mixture of $C^2Ca''O^4.H^2O$ and $C^2Ca''O^4.3H^2O$.—On adding a small quantity of chloride of calcium to a saturated solution of oxalic acid, a precipitate is formed consisting of microscopic crystalline laminæ and containing $C^2Ca''O^4.H^2O$; and on adding a small quantity of oxalic acid to a large excess of chloride of calcium, a gummy precipitate is obtained of the same composition, and appearing under the microscope as an indistinct crystalline mass; but by adding a small quantity of chloride of calcium to a very dilute solution of oxalic acid, there is formed after awhile, a precipitate consisting of square prismatic crystals of the trihydrated salt, together with oblique prismatic (monoclinic) crystals of the monohydrate, the former being in larger proportion as the oxalic acid solution is more dilute.

The square prismatic crystals of calcic oxalate occurring in plants (*Mamillaria quadrispina, Cereus senilis, Melocactus macroacanthus*, &c.), are, according to Schmid, $C^2Ca''O^4.3H^2O$; they give off two-thirds of their water, slowly when exposed to the air, more quickly in rarefied air.

A solution of calcic oxalate in hot *hydrochloric acid*, deposits crystals of the salt $C^2Ca''O^4.H^2O$ (E. Schmid). According to Souchay and Lenssen, this salt is deposited on cooling, when oxalate of calcium is added at 100°, to hydrochloric acid of specific gravity less than 1·10, in quantity sufficient to saturate it; but if the solution is not saturated, it deposits after some time, square prismatic crystals consisting of $C^2Ca''O^4.3H^2O$.—By adding oxalate of calcium to warm hydrochloric acid, of specific gravity 1·10 or higher, double salts are obtained in scaly crystals, consisting of oxalate and chloride of calcium. With acid of 1·20 specific gravity, Souchay and Lenssen obtained the salt $4C^2Ca''O^4.Ca''Cl^2.24H^2O$. Fritzsche (Pogg. Ann. xxviii. 121), by a similar process obtained an oxalato-chloride containing $C^2Ca''O^4.Ca''Cl^2.7H^2O$, which was not obtained either by Schmid, or by Souchay and Lenssen.

With *nitric acid*, oxalate of calcium behaves in the same manner as with hydrochloric acid, excepting that it is insoluble in strong nitric acid, and therefore does not yield any oxalato-nitrate (Souchay and Lenssen). According to Schmid, a solution of calcic oxalate in hot nitric acid, deposits monoclinic laminæ of the monohydrated salt, the last mother-liquors, however, yielding free oxalic acid.

**Oxalates of Cerium.** α. *Cerous Oxalate.*—Oxalic acid and alkaline oxalates added to cerous salts throw down hydrated cerous oxalate in the form of a white powder, which, when heated in a close vessel, gives off water, carbonic oxide, and carbonic anhydride, and leaves a mixture of ceroso-ceric oxide, with a small quantity of carbide of cerium (Berzelius). The salt, when prepared with cerous oxide free from lanthanum, contains 3 at. water, which it does not part with completely even at 269°. When more strongly heated, it leaves a black powder which takes fire in the air, and burns till it is converted into ceric oxide (Beringer, Ann. Ch. Pharm. xlii. 143). The salt is insoluble in water and in aqueous oxalic acid (Berzelius). It dissolves without decomposition in hot nitric acid, and crystallises out again on cooling. By leaving a solution of the salt in warm moderately strong nitric acid to evaporate slowly over caustic potash, it is obtained in well-defined rhombohedrons. No acid salt is formed. If the acid is too strong, or heated to boiling, partial decomposition takes place. (Holzmann, J. pr. Chem. lxxxiv. 81.)

*Potassio-cerous Oxalate*, $C^4K^2Ce''O^4$, is a white powder insoluble in water, and leaving when ignited a mixture of ceroso-ceric oxide and potassic carbonate (Berzelius). The insolubility of this salt affords a ready means of separating cerium from many other metals (i. 832).

β. *Ceric Oxalate* is insoluble in water, but soluble in aqueous sal-ammoniac. The solution when evaporated first deposits a yellow powder, and then yields lemon-yellow crystals. (Berzelius.)

**Oxalates of Chromium.** Neutral oxalate of ammonium forms with a solution of chromic oxide in hydrochloric acid, a pale green pulverulent precipitate.—The solution of chromic hydrate in oxalic acid prepared in the cold, has a cherry-red colour; the solution prepared at the boiling heat is green, but becomes cherry-coloured on cooling. It dries up by spontaneous evaporation to a violet-black vitreous mass, but the green solution evaporated over the water-bath yields a green mass. The solutions are not precipitated either by ammonia or by calcium-salts, but give a precipitate with lime-water, and when hot with potash.

With alkaline and earthy oxalates these solutions yield two series of double oxalates, viz.:*

$$\text{Blue salts}\quad C^6Cr'''M^3O^{12} = \left.\begin{matrix}(C^2\overset{''}{O}{}^2)^3\\ Cr'''M^3\end{matrix}\right\}O^6$$

$$\text{and}\quad C^{12}\overset{vi}{Cr}{}^2\overset{''}{M}{}^3O^{24} = \left.\begin{matrix}(C^2\overset{''}{O}{}^2)^6\\ \overset{vi}{Cr}{}^2\overset{''}{M}{}^3\end{matrix}\right\}O^{12}$$

$$\text{Red salts}\quad C^4Cr'''MO^8 = \left.\begin{matrix}(C^2O^2)^2\\ Cr'''M\end{matrix}\right\}O^4$$

$$\text{and}\quad C^8\overset{vi}{Cr}{}^2M''O^{16} = \left.\begin{matrix}(C^2\overset{''}{O}{}^2)^4\\ \overset{vi}{Cr}{}^2M\end{matrix}\right\}O^8$$

The formula of the red salts (containing alkali-metals) may also be written $C^6Cr'''M^3O^{12}$, $C^6\overset{vi}{Cr}{}^2O^{12}$. The two series of salts are analogous in composition to the acid and hyperacid oxalates of potassium, $C^2HKO^4$ (tripled) and $C^4H^3KO^8$, the 3 at. hydrogen being replaced by 1 at. triatomic chromium.

*Ammonium-salts.*—The blue salt, $C^6Cr'''(NH^4)^3O^{12}.3H^2O$, is obtained by saturating acid oxalate of ammonium with chromic hydrate, and separates on evaporation in blue scales isomorphous with the blue potassic salt (H. Kopp). It dissolves in 1½ pt. water at 15°, and in a smaller quantity of boiling water.

The *red salts* $C^4Cr'''(NH^4)O^8.4H^2O$, exactly resembles the corresponding potassium-salt, and is obtained in a similar manner.

*Argento-chromic Oxalate*, $C^6Cr'''Ag^3O^{12}.\frac{9}{2}H^2O$, is deposited in dark blue shining needles when a mixed solution of silver-nitrate and blue potassio-chromic oxalate is left to evaporate. It dissolves in 9 pts. of boiling water, and in a rather larger quantity of cold water.

*Baryto-calcic Oxalate*, $C^{12}\overset{vi}{Cr}{}^2Ba''O^{12}.4H^2O$, also with $6H^2O$. Precipitated on mixing a barium-salt with a solution of blue ammonio- or potassio-chromic oxalate. Small dark violet needles, nearly insoluble in cold water, soluble in about 30 pts. of boiling water.

*Calcio-chromic Oxalate*, $C^{12}\overset{vi}{Cr}{}^2Ca''O^{12}.6H^2O$; also with $12H^2O$. Dark violet silky needles, slightly soluble in water.

*Plumbo-chromic Oxalate*, $C^{12}\overset{vi}{Cr}{}^2Pb''O^{12}.5H^2O$. Blue precipitate formed on mixing the solutions of acetate of lead and blue potassio-chromic oxalate.

*Potassio-chromic Oxalates.*—*a. Blue salt.* $C^6Cr'''KO^8.3H^2O$.—Prepared by saturating a boiling solution of acid potassic oxalate with chromic hydrate, or by dissolving, with aid of heat, 1 pt. acid chromate of potassium, 2 pts. acid oxalate of potassium, and 2 pts. oxalic acid in 1 pt. of water. In the latter case the chromic acid is first reduced to chromic oxide by the oxalic acid, whence there results a disengagement of carbonic anhydride. The salt crystallises in large monoclinic prisms, black by reflection, and of a fine blue colour by transmitted light. The dominant faces are $\infty P$, $[\infty P\frac{3}{2}]$, $[\infty P\infty]$, $\infty P\infty$, and the prisms are terminated at the ends by the faces $\pm P$ equally developed, (like fig. 30, CRYSTALLOGRAPHY, ii. 155), or with $+P$ or $+P\infty$ predominant. Ratio of axes $a:b:c = 0{\cdot}999 : 1 : 0{\cdot}395$. Angle of axes = 86°; $+P : +P$ in the acute clinodiagonal terminal edges = 138° 48′; $-P : -P$ in the obtuse edges = 140° 34′; $+P : -P$ in the orthodiagonal terminal edges = 139° 42′; $+P : -P$ in the basal edges = 58° 19′; $\infty P : \infty P$ = about 90°; $[\infty P\frac{3}{2}] : [\infty P\frac{3}{2}]$ in the orthodiagonal principal section = 112° 30′.

The salt dissolves in 5 pts. water at 15°; the solution is green by reflection, red by transmission. If boiled and then evaporated it leaves a green amorphous residue, which however, if redissolved in water, again yields blue crystals on evaporation. The salt gives off 11 per cent. water (3 at.) at 100°.

*β. Red salt*, $C^4Cr'''KO^8.4H^2O$.—Obtained by saturating hyperacid oxalate (quadroxalate) of potassium with chromic hydrate. Crystallises in small rhomboïdal tablets or dark-red grains (Croft, Phil. Mag. [3] xxi. 197). The crystals are monoclinic, exhibiting the dominant combination $oP . \infty P . [\infty P2] . \infty P\infty . [\infty P\infty] . +P\infty . -P\infty$ Ratio of axes $a:b:c = 0{\cdot}8061 : 1 : 1{\cdot}11583$. Angle $b:c$ = 70° 33′; $\infty P : \infty P$ (clinod.) = 81° 17′; $[\infty P2] : [\infty P2]$ = 46° 27′; $oP : \infty P$ = 120° 41′; $oP : -P\infty$ = 142° 25′ (Rammelsberg, Pogg. Ann. xciii. 24). The crystals dissolve in rather more than 10 pts. of cold water; the solution in cold water is cherry-coloured: that made with boiling water is blackish-green. The solution if boiled and then left to itself for a few days, deposits garnet-red crystals, but if evaporated immediately over the water-bath, it leaves a green amorphous mass.

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* $Cr = 52{\cdot}4$; chromic chloride = $CrCl^3$.

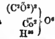
*Sodio-chromic Oxalates.* The *blue salt*, $C^6Cr'''NaO^{12}.\frac{9}{2}H^2O$, is obtained in hexagonal plates or rhomboïdal prisms by saturating a boiling solution of acid sodic oxalate with chromic hydrate. The crystals are black by reflection, deep blue by transmission, slightly efflorescent, very soluble in water (Berlin). They are monoclinic, exhibiting the combination oP . + P . − P . ∞P∞ . [∞P∞] . ∞P. Ratio of axes $a : b : c = 0·7218 : 1 : 0·8803$. Angle $b : c = 79° 20'$; oP : + P = 120°; oP : − P = 128° 12'; oP : ∞P = 96° 20'; ∞P : ∞P (clinod.) = 73° 25'. Cleavage perfect parallel to oP. (Rammelsberg.)

According to Rammelsberg, a solution of chromic hydrate in acid sodic oxalate yields first a red and afterwards a blue sodio-chromic oxalate, the two salts having the same composition (?), and the red salt also forming monoclinic crystals.

OXALATES OF COBALT. α. *Cobaltous salts.—Neutral cobaltous oxalate*, $C^2Co''O^4.2H^2O$, obtained by digesting the carbonate with excess of oxalic acid, is a rose-red powder, nearly insoluble in water and oxalic acid, easily soluble in aqueous ammonia. A blue *basic salt*, $C^2Co''O^4.2Co''H^2O^2$, is obtained by treating cobaltous oxalate with boiling aqueous oxalate.

A *potassio-cobaltous oxalate* is obtained in rose-coloured rhomboïdal crystals insoluble in water, by dissolving cobaltous oxalate in a boiling solution of the neutral potassic salt. Cobaltous oxalate dissolves also in a hot solution of the acid ammonium-salt; but the liquid when left to evaporate deposits rose-coloured sparingly soluble crystals containing only a small quantity of cobalt.

*Oxalate of Cobalt-nickel-ammonium*, $2[C^4(Co''N^2H^6)''(Ni''N^2H^6)''O^8].9H^2O$, was obtained by Rautenberg (Ann. Ch. Pharm. cxiii. 360) in separating nickel and cobalt by Laugier's method (i. 1039), being deposited after some weeks from the ammoniacal solution from which the greater part of the nickel-oxalate had previously separated. It forms transparent cherry-red triclinic prisms which give off all their water of crystallisation at 100°, crumbling to a brick-red powder, and ammonia at 180°. It is insoluble in water, easily soluble in ammonia, the solution when left to evaporate, depositing oxalate of nickel-ammonium while a cobalt-salt remains in solution.

β. *Cobaltic salts.* A solution of cobaltous oxalate in strong aqueous ammonia left to evaporate in contact with the air deposits large deep-red crystals containing, according to L. Gmelin (*Handbook*, ix. 162) $3Co^2O^3.12NH^3.Co^2O^3.3H^2O$, which may be represented by the formula  $\left.\begin{matrix}(C^2\overset{''}{O}{}^2)^3\\ \overset{''}{Co}{}^2\\ H^{36}\end{matrix}\right\}O^6$ $.3H^2O$. The crystals are sparingly soluble in water and in aqueous ammonia, and when boiled with potash, give off ammonia and deposit brown peroxide of cobalt.

Other ammoniacal cobaltic oxalates are described under COBALT-BASES, AMMONIACAL (i. 1051).

OXALATES OF COPPER. *Neutral cupric Oxalate*, $2C^2Cu''O^4.H^2O$ (according to Löwe, Jahresb. 1860, p. 243), is a light greenish-blue precipitate, insoluble in water, nearly or quite insoluble in oxalic acid, but easily soluble in the neutral oxalates of ammonium, potassium and sodium. It does not give off the whole of its water even at 120°, but decomposes at a somewhat higher temperature.

*Ammonio-cupric Oxalate*, $C^4(NH^4)^2Cu''O^8.2H^2O$, obtained by dissolving cupric oxalate in the neutral ammonium-salt, or cupric oxide in the acid ammonium-salt, forms dark blue rhombic plates permanent in the air, sparingly soluble in water, with partial decomposition.

*Oxalate of Cuprammonium*, $C^2(N^2H^6Cu'')''O^4.H^2O$, is obtained, by evaporating an ammoniacal solution of cupric oxalate, in short flattened hexagonal prisms, of a dark-blue colour: it effloresces on exposure to the air, giving off water and ammonia.

*Oxalate of Copper and Cuprammonium*, $C^4Cu''(N^2H^6Cu'')''O^8$, is deposited as a sky-blue crystalline powder when ammonia is treated with a larger quantity of cupric oxalate than it is capable of dissolving.

*Lithio-cupric Oxalate*, $C^4Li^2Cu''O^8.2H^2O$, is deposited in blue crystals by spontaneous evaporation of the solution obtained by boiling acid lithic oxalate with cupric oxide; when redissolved in water, it suffers partial decomposition (Troost, Ann. Ch. Phys. [3] li. 103).

*Potassio-cupric Oxalate* crystallises in blue rhombohedrons, $C^4K^2Cu''O^8.2H^2O$, sparingly soluble in water, or in flattened needles containing $C^4K^2Cu''O^8.4H^2O$. It is decomposed by boiling water, with separation of cupric oxalate.

*Sodio-cupric Oxalate*, $C^4Na^2Cu''O^8.2H^2O$, forms dark sky-blue often flattened needles

OXALATE OF DIDYMIUM. $C^2Di''O^4.H^2O$; also with $4H^2O$.—Pulverulent and white, with a slight tinge of rose-colour, when precipitated from neutral solutions; but when redissolved by the aid of heat in excess of nitric or hydrochloric acid, it separates as the liquid cools, in the granular and crystalline state, sometimes even in small, rose-coloured, rectangular prisms terminated by four-sided pyramids with their faces resting on the edges of the prism. This salt is completely insoluble in water, and nearly insoluble in oxalic acid and in very dilute mineral acids. The air-dried salt (with 4 at. water) gives off about 20 per cent. water at 100°, leaving the monohydrated salt. (Marignac, Ann. Ch. Phys. [3] xxxviii. 175.)

Oxalate of Glucinum remains, when its aqueous solution is evaporated, as a transparent gummy mass, possessing the sweetest taste of all glucinum-salts. (Vauquelin.)

*Ammonio-glucinic Oxalate*, $C^4(NH^4)^2G''O^8$, forms trimetric crystals exhibiting the combination $\infty\breve{P}\infty \,.\, \infty\bar{P}\infty \,.\, oP \,.\, P \,.\, 2P \,.\, \infty P \,.\, P\infty \,.\, P\infty \,.\, 2\breve{P}\infty \,.\, 4\bar{P}\infty$. Ratio of axes $a : b : c = 0{\cdot}8759 : 1 : 1{\cdot}7413$. Inclination of the faces, P : P in the brachydiagonal principal section = 121° 50′; in the macrodiagonal = 111° 24′; in the basal section = 98° 44′; 2P : 2P in these three sections = 105° 56′; 93° 10′ and 132° 4′; $-\infty P : \infty\bar{P}\infty = 138° 47'$; $oP : \breve{P}\infty = 143° 27'$; $oP : \bar{P}\infty = 139° 45'$. (Sénarmont, Jahresb. 1857, p. 295.)

Oxalates of Iron. α. *Ferrous salts.*—Ferrous oxalate occurs as *oxalite* or *humboldtine*, $2C^2Ffe''O^8.3H^2O$, in deposits of lignite. It is very soft, and crumbles between the fingers, has a density of 2·13 — 2·489, yellow colour, dull or slightly resinous lustre, and when insulated acquires negative electricity by friction. When thrown on red-hot coals it emits a strong vegetable odour and leaves a residue which is attracted by the magnet. It is found in lignite at Kolosoruk in Bohemia, at Gross-Almerode in Hessia, and in shale at Cape Ipperwash in Upper Canada (Dana, ii. 465). It appears to have been formed by the decomposition of succulent plants.

Iron dissolves in oxalic acid, with evolution of hydrogen, and the liquid which has a sweet astringent taste, gradually deposits ferrous oxalate as a light-yellow powder. This salt separates also in small shining yellow crystals containing $C^2Ffe''O^4.2H^2O$, when ferrous sulphate is precipitated by oxalic acid or neutral oxalate of potassium; also when a solution of ferric oxide in oxalic acid is exposed to sunshine. It is nearly insoluble in cold, very sparingly soluble in boiling water. According to Souchay and Lenssen, the dihydrated salt dissolves in 4,500 pts. of cold and 3,800 pts. of hot water.

When the dihydrated salt is heated with the strongest sulphuric acid ($H^2SO^4$) carbonic oxide and carbonic anhydride are evolved and pure ferrous sulphate remains in the form of a soft white powder. But if the same salt be heated with dilute sulphuric acid, the liquid after cooling yields crystals of oxalic acid, and ferrous sulphate remains in solution.—When ferrous oxalate is dissolved to saturation in strong hydrochloric acid at a boiling heat, the liquid when quite cold, deposits large transparent crystals of oxalic acid, and afterwards crystals of ferrous chloride. (Souchay and Lenssen.)

If ferrous oxalate be added to boiling solution of caustic potash, the boiling heat being continued for some time, a velvet-black precipitate of ferrous oxide is produced, which however soon passes on the filter to a higher state of oxidation. Ferrous oxalate boiled with a concentrated solution of acid carbonate of potassium, yields a perfectly white precipitate of ferrous carbonate, which likewise oxidises quickly during washing. (Böttger, J. pr. Chem. lxxvi. 238.)

*Acid salt?* A solution of iron in oxalic acid, yields before complete saturation, greenish-yellow, very soluble, efflorescent prisms which appear to be an acid ferrous oxalate, or according to Barreswil, a *ferroso-ferric oxalate.*

*Potassio-ferrous Oxalate.* $C^4K^2Ffe''O^8.2H^2O$.—A solution of ferrous oxalate in oxalate of potassium, deposits, when mixed with alcohol and left to stand for 24 hours, oily drops of this double salt which soon solidify. (Souchay and Lenssen.)

β. *Ferric salts.* When ferric hydrate is treated with a quantity of aqueous oxalic acid not sufficient to dissolve it, a yellow powder is formed nearly insoluble in water, and apparently consisting of neutral ferric oxalate. The same salt is precipitated on adding a small quantity of neutral potassic oxalate to a ferric salt. It dissolves in oxalic acid, forming a solution which, when exposed to sunshine, gradually assumes a greenish-yellow colour, gives off carbonic anhydride, and deposits crystals of ferrous oxalate till it becomes quite colourless.

Ferric hydrate dissolves in the acid oxalates of the alkali-metals, forming double salts.

*Ammonio-ferric Oxalate*, $C^6(NH^4)^3Fe'''O^{12}$.—A hot solution of ferric hydrate in acid oxalate of ammonium deposits this salt on cooling in small, anhydrous, rhombic octahedrons, having a greenish-white colour and turning yellow when exposed to light. The salt dissolves in 1·1 pt. water at 20° and in 0·79 pt. boiling water. The aqueous solution exposed to sunshine gives off carbonic anhydride, and deposits ferrous oxalate in the form of a yellow powder.

*Baryto-ferric Oxalate*, $C^{12}\overset{''}{Ba}{}^3\overset{'''}{Fe}{}^2O^{24}.6H^2O$ (?), is precipitated on mixing a concentrated solution of the ammonio-ferric salt with chloride of barium. The precipitate crystallises from boiling water in greenish-yellow silky needles.

*Calcio-ferric Oxalate* is an uncrystallisable precipitate.

*Potassio-ferric Oxalate*, $C^6K^3Fe'''O^{12}.3H^2O$, crystallises in flattened prisms or scales of an emerald-green colour, which effloresce in dry air, and decompose quickly when exposed to light, depositing ferrous oxalate. It is isomorphous with the blue potassio-chromic oxalate. (H. Kopp.)

*Sodio-ferric Oxalate*, $C^6Na^3Fe'''O^{12}.3H^2O$, also forms green crystals moderately soluble in water. The crystals are monoclinic, the dominant faces being $oP$, $+P$, $-P$, $\infty P$. Ratio of axes $a : b : c = 0·7304 : 1 : 0·877$. Angle $b : c = 79° 44'$, $\infty P : \infty P$ (clinod.) $= 73° 10'$; $+P : +P$ (clinod.) $= 91° 12'$; $-P : -P$ in the same $= 101° 22'$; $+P : -P$ (basal) $= 111° 43'$ : $oP : +P = 119° 58'$; $oP : -P = 128° 19'$. Cleavage easy parallel to $oP$. (Rammelsberg.)

*Strontio-ferric Oxalate* is an uncrystallisable precipitate.

OXALATE OF LANTHANUM. $C^2La''O^4$.—White precipitate insoluble in water, nearly insoluble in oxalic acid, easily soluble in nitric acid, separating from this solution like the cerous salt (p. 255) in well-defined rhombohedrons. (Holzmann.)

OXALATES OF LEAD.—The *neutral salt*, $C^2Pb''O^4$, is a white precipitate insoluble in water and in acetic acid, but soluble in nitric acid. It dissolves also at the boiling heat in aqueous chloride, nitrate, and succinate of ammonium, but is insoluble in caustic ammonia, and in the carbonate. The dry salt heated in a retort placed in an oil-bath, decomposes at about 300°, giving off a mixture of 3 vol. $CO^2$ to 1 vol. CO, and leaving a residue of suboxide of lead. (Pelouze, Ann. Ch. Phys. [3] iv. 104):

$$2C^2Pb''O^4 \quad = \quad 3CO^2 \quad + \quad CO \quad + \quad Pb^2O.$$

A *basic oxalate of lead*, $C^2Pb''O^4.2Pb''O$, is obtained as a white powder by precipitating a solution of basic acetate of lead with neutral oxalate of ammonium, or by boiling neutral oxalate of lead with the basic acetate (which is thereby converted into neutral acetate). It is precipitated in small shining laminæ on mixing a boiling solution of oxamide with nitrate or acetate of lead containing a little ammonia. It absorbs carbonic acid from the air, and is ultimately converted into a mixture of carbonate and neutral oxalate of lead.

*Potassio-plumbic Oxalate.*—Acid oxalate of potassium digested with hydrate of lead dissolves a small portion of it, and the solution yields small needles which are permanent in the air, but are decomposed by alkalis. (Wenzel.)

*Oxalato-nitrates of Lead.*—*a.* The *normal salt*, $C^2Pb''O^4.N^2Pb''O^6.2H^2O = \left.\begin{matrix}\overset{''}{Pb}{}^2\\(C^2O^2)''\\(NO^2)^2\end{matrix}\right\}O^4$ $.2H^2O$, is produced by pouring a solution of neutral lead-acetate into a mixture of dilute oxalic and a large quantity of nitric acid, or dilute oxalic acid into a mixture of dilute lead-acetate and nitric acid; also when oxalate of lead is dissolved in dilute nitric acid, or boiled with a strong solution of lead-nitrate. It forms rhombic or hexagonal plates having a nacreous lustre; is slowly decomposed by cold, quickly by boiling water. (Johnston, Phil. Mag. [3] xiii. 25.—Dujardin, J. pr. Chem. xv. 308.)

*β.* A *basic salt*, $C^2Pb''O^4.3N^2Pb''O^6.2Pb''O.3H^2O \quad = \left.\begin{matrix}\overset{''}{Pb}{}^6\\(C^2O^2)''\\(NO^2)^6\end{matrix}\right\}O^{10}.3H^2O$, is formed when oxamide is boiled with a strong solution of lead-nitrate mixed with ammonia, and separates in white shining crystalline grains, which must be washed with cold water and dried in a vacuum. If the boiling be too long continued, while the liquid still contains neutral nitrate of lead (which thereby becomes basic), the salt *β* is converted into *a*. The salt *β* is also formed when basic oxalate of lead is boiled with a solution of lead-nitrate in a double quantity of water, the ebullition being stopped before *β* is converted into *a*. (Pelouze, Ann. Ch. Phys. [2] lxxix. 104.)

OXALATES OF LITHIUM.—The *neutral salt*, $C^2Li^2O^4$, obtained by saturating a hot solution of oxalic acid with carbonate of lithium, separates on cooling in indistinct nodulous anhydrous crystals; it also separates in the anhydrous state from its aqueous solution on addition of alcohol. 1 pt. of it dissolves in in 13·1 pts. water at 19·5°.

The *acid salt*, $C^2HLiO^4.H^2O$, forms large tabular crystals which dissolve in 12·8 pts. water at 17°, give off their water of crystallisation at 100°, and oxalic acid at 160°. (Souchay and Lenssen.)

OXALATES OF MAGNESIUM, $C^2Mg''O^4$. This salt is best prepared by neutralising oxalic acid with carbonate of magnesium and washing with cold water; when precipitated from a magnesium-salt by oxalate of potassium, it always retains a portion of that salt. Prepared by the first method, it is a white sandy powder consisting of

$C^2Mg''O^4.2H^2O$, soluble in 1500 pts. of water at 16° and 1300 pts. of boiling water. It gives off 1·5 per cent. water at 100°, and does not lose the whole of it even at 140°; but at 150° it becomes anhydrous, at the same time, however, suffering partial decomposition.

No acid oxalate of magnesium or double oxalate of magnesium and sodium appears to exist.

*Ammonio-magnesian Oxalates.*—A concentrated solution of chloride of magnesium forms, with oxalate of ammonium, a precipitate of oxalate of magnesium, which always contains small quantities of the double oxalate of magnesium and ammonium. But a dilute solution of chloride of magnesium mixed with oxalate of ammonium, especially if a little caustic ammonia is added, yields, after standing for some time, crystalline crusts, consisting of oxalate of magnesium and ammonium and oxalate of ammonium in equivalent proportions, varying according as the magnesia or the oxalate of ammonium predominated in the liquid; they dissolve in water with separation of oxalate of magnesium.

α. $C^4Mg''(NH^4)^2O^8.5C^2(NH^4)^2O^4.9H^2O$.—Obtained by adding oxalate of ammonium to a magnesia solution, rendered strongly alkaline by ammonia, and then mixed with a quantity of sal-ammoniac sufficient to redissolve the precipitate,—in such proportion, that the magnesia may be to the oxalic acid ($C^2H^2O^4.2H^2O$), as 1 : 12·6. (Souchay and Lenssen.)

β. $5C^4Mg''(NH^4)^2O^8.8C^2(NH^4)^2O^4.24H^2O$.—By mixing a magnesia solution with oxalate of ammonium, in such proportion that the magnesia may be to the oxalic acid, as 1·0 : 6·3. (Souchay and Lenssen.)

γ. $C^4Mg''(NH^4)^2O^8.4C^2(NH^4)^2O^4.8H^2O$ (Souchay and Lenssen); with $2H^2O$ (Kayser, Pogg. Ann. lx. 143).—Prepared by gradually adding recently precipitated oxalate of magnesium to a boiling concentrated solution of oxalate of ammonium, till the former no longer dissolves, even after long boiling. On filtering hot, and leaving the liquid to cool quietly, the salt γ, separates in hard, warty, crystalline crusts, having the appearance of enamel, slightly translucent, and efflorescing in the air. It dissolves pretty readily in water, with partial separation of oxalate of magnesium; in ammoniacal salts it forms a clear solution.—At 100° it gives off 13·3 per cent. (rather more than 6 at.) water; at 120°, 7 at. in all; at 140° it begins to decompose and assume a brownish tint. (Souchay and Lenssen.)

δ. $C^4Mg''(NH^4)O^8.6C^2(NH^4)^2O^4.8H^2O$.—When the mother-liquor from which the preceding salt has crystallised is mixed with a little water and ammonia, and set aside for some weeks in the cold, it deposits milk-white crusts, which dissolve in water with partial decomposition, the solution becoming turbid. It gives off 12·15 per cent. (about 8 at.) water at 100°. (Souchay and Lenssen.)

ε. $C^4Mg''(NH^4)^2O^8.2C^2Mg''O^4.2H^2O$ or $C^8Mg''^3(NH^4)^2O^{16}.2H^2O$, is produced, according to Brandes (Schw. J. xxvii. 18), when aqueous chloride of magnesium is mixed with neutral oxalate of ammonium, especially in presence of excess of ammonia, and is gradually deposited in crystalline crusts. Souchay and Lenssen did not succeed in preparing this salt.

*Potassio-magnesic Oxalate*, $C^4K^2Mg''O^8.6H^2O$.—Deposited in white needles when a strong solution of neutral potassic oxalate is boiled with recently precipitated oxalate of magnesium, and the filtered liquid is left to cool. It effloresces quickly in the air, is insoluble in cold water, and is decomposed by hot water with separation of oxalate of magnesium. (Kayser, *loc. cit.*)

OXALATE OF MANGANESE.—This salt, whether prepared by precipitating the sulphate or chloride of manganese with oxalic acid, or by treating the carbonate of manganese or manganoso-manganic oxide with oxalic acid, contains, in the air dried state, $\frac{5}{2}$ at. water. Souchay and Lenssen (Ann. Ch. Pharm. cii. 47) found in it, 37·55 per cent. MnO, the formula $2C^2Mn''O^4.5H^2O$ requiring 37·83 per cent. 1 pt. of this hydrated salt dissolves in 2460 pts. of cold, and in 1250 pts. of boiling water; but the solubility is very greatly increased by the presence of a trace of potassic or ammonic oxalate. At 100°, according to Souchay and Lenssen, it gives off all its water (as previously found by Liebig, Ann. Ch. Pharm. xcv. 116).

These results are at variance with those obtained by other chemists. According to Graham, the salt contains $\frac{5}{2}$ at. water, the whole of which it retains at 100°; according to Hausmann and Löwenthal it contains, after drying at 100°, 2 at. water.

According to H. Croft (Chem. Gaz. 1857, p. 62) the quantity of water contained in manganous oxalate varies with the temperature at which it is precipitated. Hot concentrated solutions of manganous sulphate and oxalic acid yield a white granular precipitate consisting of $C^2Mn''O^4.2H^2O$, which does not give off any water at 100°. (This agrees with the statement of Hausmann and Löwenthal.) In a solution of manganous sulphate in 30 pts. of water, oxalic acid produces a precipitate which has a faint violet colour, but in a few days becomes white and granular, and exhibits the same composition. When manganous sulphate dissolved in 30 to 100 pts. of water is precipitated by oxalate potassium, a pale violet crystalline precipitate is obtained, resembling benzoic acid and containing $C^2Mn''O^4.3H^2O$. It is unalterable in the air at ordinary temperatures, but at 100° gives off 1 at. water and turns white. When heated for some time in the air, it yields red crystalline manganic oxide (**Croft**).—These statements are confirmed by **Gorgeu** (Compt. rend. xlvii. 929). Oxalic acid mixed with excess of manganous sulphate in the cold, yields rose-coloured prismatic needles of the salt $C^2Mn''O^4.3H^2O$; but when a very hot solution of oxalic acid is mixed with a hot solution of a manganous salt till a precipitate begins to form, and the liquid is then left to cool, white flattened octahedrons are obtained, consisting of $C^2Mn''O^4.2H^2O$.—The red salt, when dried in the air, gives off 1 at. water and turns white; but in vacuo and even at 95°, it retains its red colour, although it loses the greater part of its water.

*Ammonio-manganous Oxalate.*—Oxalate of manganese forms, with oxalate of ammonium, a series of double salts varying in composition according to the degree of dilution and the proportions in which the constituent salts are mixed.

α. $C^4Mn''(NH^4)^2O^8.2H^2O$ is obtained by adding oxalate of manganese to a boiling saturated solution of oxalate of ammonium, and filtering the rose-coloured solution while still hot. The crystalline crusts composed of microscopic square prisms, which first separate from the liquid, consist of the salt *a*. The mother-liquor yields crystals of different composition. (**Souchay** and **Lenssen.**)

β. $C^4Mn''(NH^4)^2O^8.C^2(NH^4)^2O^4.4H^2O$.—The mother-liquor of the salt α, filtered and left to itself for twenty-four hours, deposited crystalline crusts consisting of microscopic prisms which gave by analysis 15·24 per cent. MnO and 46 20 $C^2O^3$, the formula of salt β requiring 15.37 MnO and 46·63 $C^2O^3$.

γ. $C^4Mn''(NH^4)^2O^8.4C^2(NH^4)^2O^4.8H^2O$.—The mother-liquor of β mixed with water, yielded, after standing for a day, crystalline crusts containing 7·44 per cent. MnO and 47·48 per cent. $C^2O^3$; the formula γ requires 7·84 per cent. MnO and 47·57 $C^2O^3$.

δ. The mother-liquor of γ deposits, after standing for some time, crystalline crusts containing 6·19 per cent. MnO and 49·82 $C^2O^3$, agreeing with the formula $C^4Mn''(NH^4)^2O^8.C^2(NH^4)^2O^4.8H^2O$, which requires 6·17 MnO and 49·86 $C^2O^3$.

All these salts are decomposed by water and effloresce rapidly in the air. The colour is reddish or white according to the proportions of manganese contained in them. Those which contain a large proportion of manganese separate in small prisms, while those with a smaller quantity of manganese are deposited in crystalline crusts or nodules, and always after the solution has been left at rest for some time. (**Souchay** and **Lenssen.**)

ε. *Oxalate of Manganese and Manganammonium.* $C^4Mn''(N^2H^6Mn'')''O^8.6H^2O$.—When a boiling solution of oxalate of ammonium is saturated with oxalate of manganese, the liquid filtered, and ammonia added till the filtrate smells slightly of it, a white or slightly green crystalline powder is precipitated, consisting of transparent microscopic crystals, which have the form of square prisms, but are so much truncated that they are scarcely distinguishable from cubes. (**Souchay** and **Lenssen.**)

**Winkelblech** assigned to a salt prepared in a similar manner, the formula $4NH^3.C^4Mn''(NH^4)^2O^8.2C^2Mn''O^4.8H^2O$, the accuracy of which is called in question by **Gmelin** (*Handbook*, ix. 147). The salt decomposes quickly in contact with water, turning brown and absorbing oxygen. At 100° it gives off 6 at. water, assuming at the same time a faint brown colour. (**Souchay** and **Lenssen.**)

*Potassio-manganous Oxalate.* $C^4Mn''K^2O^8.2H^2O$.—Obtained in reddish crusts by adding manganous oxalate to a boiling concentrated solution of oxalate of potassium, and leaving the filtrate to cool. Gives off all its water at 100°. (**Souchay** and **Lenssen.**)

*Potassio-manganic Oxalate* is best obtained by saturating 3 pts. of oxalic acid with carbonate of potassium, adding 4 pts. of oxalic acid, and then peroxide of manganese till the liquid exhibits but a faint acid reaction. The purple liquid thus formed is very easily decomposed by light and heat. Mixed with alcohol in the dark and in a vessel externally cooled, it deposits potassio-manganic oxalate (probably $C^6Mn'''K^3O^{12}.3H^2O$), in purple-red crystals which however cannot be dried without decomposition. (**Souchay** and **Lenssen.**)

*Sodio-manganous Oxalate.* Oxalate of manganese dissolves pretty freely in warm oxalate of sodium, and the solution deposits crystalline crusts containing variable quantities of manganese, and probably consisting of sodic-oxalate having oxalate of manganese mechanically inclosed within it (**Souchay** and **Lenssen.**)

OXALATES OF MERCURY.—α. *Mercurous Oxalate*, $C^2Hg^2O^4$, is obtained in the anhydrous state by heating mercuric oxalate to 164°. It is also produced by heating mercurous nitrate with excess of oxalic acid, as a white precipitate, which is insoluble even in hot water, and obstinately retains hygroscopic water, from which indeed, it cannot be freed without decomposing into mercuric oxalate and metallic mercury; this decomposition taking place at 100°. The same products are obtained when mercurous oxide is heated with oxalic acid.—The anhydrous salt obtained by the first method, begins to decompose only at 175° (Souchay and Lenssen). According to Harff (N. Br. Arch. v. 264) mercurous oxalate obtained by precipitation and dried at 100° contains $C^2Hg^2O^4.H^2O$.

Mercurous oxalate is insoluble in oxalic acid, easily soluble in hot nitric acid; in cyanide and sulphocyanate of potassium, it dissolves very easily, with separation of metallic mercury; it is also somewhat soluble in ammonia-salts. Heated with oxalate of potassium, sodium, or ammonium, it forms double mercuric oxalates, with separation of mercury. It detonates when heated.—With ammonia it forms a greyish-black powder, supposed by Harff to be $3Hg^2O.2NH^3.C^2O^3$; it does not however appear to be of constant composition. (Souchay and Lenssen.)

*Mercuric Oxalate.* $C^2Hg''O^4$.—Obtained pure as a white amorphous powder, by adding a solution of mercuric nitrate to excess of oxalic acid, or by prolonged digestion of yellow mercuric oxide with oxalic acid (Souchay and Lenssen). It is decomposed by heat, giving off carbonic anhydride and metallic mercury. When dry, it detonates violently on being rubbed. It is easily soluble in hydrochloric acid, less soluble in cold nitric acid, insoluble in oxalic acid. Decomposed by carbonate and phosphate of sodium. Heated with solution of sal-ammoniac, it gives off carbonic anhydride, and yields oxalate of ammonium and mercurous chloride. (Souchay and Lenssen.)

*Ammonio-mercuric Oxalate.* $C^4Hg''(NH^4)^2O^8.2H^2O$.—Precipitated on adding recently precipitated mercuric oxalate to a boiling concentrated solution of neutral oxalate of ammonium, in white microscopic needles, easily decomposed by light and heat. Loses 12·5 per cent. of its weight at 100°, and decomposes with a hissing noise at a higher temperature, leaving no residue. It is decomposed by water, and does not dissolve in alcohol or ether. (Souchay and Lenssen.)

*Oxalate of Tetra-mercurammonium* has been already described (iii. 918).

*Potassio-mercuric Oxalate.* $C^4Hg''K^2O^8.2H^2O$.—Prepared like the preceding. Small white, beautifully iridescent crystalline scales, which under the microscope appear like square prisms. It is decomposed by water gives off water; and turns black at 100°; and is partially decomposed by light. (Souchay and Lenssen.)

Mercuric oxalate does not dissolve in oxalate of sodium.

OXALATE OF MOLYBDENUM (Berzelius, Pogg. Ann. vi. 348). *Molybdous Oxalate.*—Dark grey precipitate, which turns black when dried, and is sparingly soluble in excess of oxalic acid.

*Potassio-molybdous Oxalate* is purple and soluble in water.

*Molybdic Oxalate* crystallises in blackish-blue crystals when the aqueous solution is left to evaporate spontaneously. From its solution in water, which is red, ammonia throws down a pale brick-red, *basic salt* insoluble in excess of ammonia.

*Potassio-molybdic Oxalate* formed by digesting molybdic hydrate in salt of sorrel is soluble in water. (Berzelius.)

*Molybdoso-molybdic Oxalate.* Blue oxide of molybdenum dissolves in oxalic acid, forming a blue solution which leaves a blue mass when evaporated, becomes green when diluted with a small quantity of water, but brown on being mixed with a large quantity. (Heyer, Crell. Ann. 1784, ii. 14.)

*Oxalato-molybdic acid* is formed by digesting molybdic trioxide with aqueous oxalic acid. The solution, which is colourless even when the molybdic acid is in excess, yields on evaporation a colourless jelly which becomes crystalline without further dessication, dissolves in water, and with yellow colour in alcohol (Berzelius.) The aqueous solution of salt of sorrel readily dissolves molybdic acid, forming a non-crystallisable *oxalato-molybdate of potassium.* (Berzelius.)

OXALATE OF NICKEL, $C^2Ni''O^4.2H^2O$. Greenish-white precipitate insoluble in water, soluble in ammonia and in ammoniacal salts. It dissolves also in potash, forming a crystallisable *potassio-nickel-oxalate.*

Neutral oxalate of ammonium dissolves oxalate of nickel, and the solution yields by evaporation green prisms of *ammonio-nickel-oxalate.* On adding to the aqueous solution of this salt a small quantity of ammonia, a pale green precipitate is formed, consisting, according to Winckelblech (Ann. Ch. Pharm. xiii. 278), of *oxalate of nickel and nickel-ammonium*, $C^4Ni''(N^2H^6Ni'')''O^8.6H^2O$.

*Oxalate of Nickel-cobalt-ammonium*, (see p. 258).

OXALATE OF PALLADIUM.—Alkaline oxalates added to a solution of palladious nitrate, form a light yellow precipitate.

*Ammonio-palladious Oxalate*, $C^4Pd''(NH^4)^2O^8.2H^2O$, obtained by dissolving hydrate or carbonate of palladium in acid oxalate of ammonium, crystallises in bronze-yellow rhomboïdal prisms containing 2 at. water, or sometimes in needles containing 8 at. water.

OXALATES OF PLATINUM. *a. Platinous salt.*—Platinate of sodium dissolves in warm aqueous oxalic acid, carbonic anhydride being evolved, and the platinic oxide reduced to platinous oxide. The solution, which has first a red, then a violet, and ultimately a deep indigo colour, deposits dark copper-coloured needles, which were supposed by Döbereiner (who did not analyse them) to be platinous oxalate; but, according to Souchay and Lenssen, they contain 44·4 per cent. platinous oxide, and 12·00 soda, agreeing nearly with the formula of *sodio-platinous oxalate*, $C^4Na^2Pt''O^8.2H^2O$. This salt, when moist, is decomposed by exposure to the air; it dissolves in hot water, forming a greenish solution, which becomes blue on evaporation, and is decolorised by hydrochloric acid. It is insoluble in alcohol and in ether (Souchay and Lenssen). It explodes when heated. (Döbereiner.)

β. *Platinic salt.*—According to Bergmann, the precipitate formed by soda in solution of platinic chloride dissolves in oxalic acid, forming a yellow solution which yields crystals of the same colour; but they have not been analysed.

The oxalates of the platinammoniums will be described under Platinum-bases.

Oxalates of Potassium. α. *Neutral salt*, $C^2K^2O^4.H^2O$.—Obtained by saturating either of the acid salts with carbonate of potassium. It forms transparent crystals very soluble in water, insoluble in alcohol, and giving off their water (9·7 per cent.) at 160°. The crystals are monoclinic, and often have their faces twisted, so that they exhibit concavities and convexities. Dominant faces, $+P . -P . \infty P\infty . +P\infty . -P\infty . oP$. Ratio of axes, $a : b : c = 0·6748 : 1 : 1·1572$. Angle of axes, $b : c = 69·5°$; $+P\infty : \infty P\infty = 130° 35'$; $-P\infty : \infty P\infty = 148° 20'$; $+P\infty : oP = 118° 40'$; $-P\infty : oP = 142° 10'$; $-P : oP = 126° 10'$; $+P : oP = 106° 54'$; $+P : -P = 127° 10'$; $+P : \infty P\infty$ 113° 35'; $-P : \infty P\infty$ = about 129° (De la Provostaye, Ann. Ch. Phys. [3] iv. 454). According to Bérard, neutral potassic oxalate sometimes crystallises with 3 at. water.

β. *Acid salt, Dioxalate* or *Binoxalate of Potassium, Salt of Sorrel*, $C^2HKO^4$.—This salt is contained in the juice of various species of *Rumex* and *Oxalis*, whence it may be extracted by clarifying the juice with clay, white of egg, or bullock's blood, and leaving the clear liquor to crystallise; it is prepared by this process in large quantities in the Black Forest. It may also be prepared by partially neutralising oxalic acid with carbonate of potassium. It forms transparent crystals which have a sour taste, redden litmus, dissolve sparingly in cold water, and in 14 pts. of boiling water (Wenzel); in 4 pts. of boiling water (*Weltzien's Syst.*); in 40 pts. of cold and 6 pts. of boiling water (*Berz. Lehrb.*), nearly or quite insoluble in cold alcohol, soluble in 34 pts. of boiling alcohol (see Storer's *Dictionary of Solubilities*, p. 428).

The crystals of salt-of-sorrel are commonly said to contain 1 at. water; $C^2HKO^4 H^2O$. According to De la Provostaye (*loc. cit.*) they probably belong to the trimetric system, having their axes in the ratio 0·9494 : 1 : 4·123 and exhibiting the combination $\breve{P}\infty . \infty\bar{P}\infty . \infty\breve{P}\infty . \bar{P}\infty . P\frac{2}{7} . P\frac{4}{7}$. Angle $\breve{P}\infty : \infty\breve{P}\infty = 103° 38'$; $\infty\breve{P}\infty : \breve{P}\infty = 133° 26'$; $\bar{P}\infty : \bar{P}\infty = 132°$; $\bar{P}\infty : P\frac{4}{7} = 130° 35'$; $\bar{P}\infty : P\frac{2}{7}$ = about 149° 50'; $\breve{P}\infty : P\frac{4}{7} = 127° 50$.

According to Rammelsberg (Pogg. Ann. xciii. 24), the crystals obtained by half saturating oxalic acid with carbonate of potassium contain $4C^2HKO^4.H^2O$, and are trimetric, having their axes $a : b : c = 0·9478 : 1 : 0·5875$,* and exhibiting the combination $P : 2P . \infty P . \infty P\infty . oP : 7\breve{P}\infty$, only half of the pyramidal and prismatic faces however, being commonly present. Angle $oP : 7\breve{P}\infty = 103° 40'$; $7\breve{P}\infty : 7\breve{P}\infty$ (basal) = 152° 40'; $2P : \infty P = 149° 39'$; $P : oP = 139° 30'$. Cleavage perfect parallel to oP.

According to Marignac (*Recherches sur les formes cristallines de quelques composés chimiques*, Genève 1855; Jahresb. 1855, p. 462), the ordinary crystals of salt-of-sorrel are anhydrous ($C^2HKO^4$), and belong to the monoclinic system exhibiting the combination $\infty P . \infty P\infty . [\infty P\infty] . oP . [P\infty] . [2P\infty] . P . +2P2 + \frac{1}{2}P\infty$. Angle $\infty P : \infty P$ (clinod.) = 152° 36'; $[P\infty] : [P\infty]$ (clinod.) = 119° 40; $[2P\infty] : [2P\infty]$ (clinod.) = 81° 24'; $oP : \infty P\infty = 133° 29'$; $oP : \infty P = 131° 57'$; $[\infty P\infty] : [P\infty] = 120° 10'$; $[\infty P\infty] : +2P2 = 122° 13'$.† Cleavage very easily parallel to $\infty P\infty$; less easily parallel to $[\infty P\infty]$.

In preparing potassio-antimonic oxalate (p. 252), Rammelsberg obtained crystals of acid potassic oxalate containing $2C^2HKO^4.H^2O$. These crystals, which effloresced very quickly, were trimetric prisms exhibiting the combination $\infty P . \infty\breve{P}2 . \infty\breve{P}\infty . P . 3\breve{P}3$. Ratio of axes, $a : b : c = 0·4590 : 1 : 6·1959$. Angle $\infty P : \infty P = 130° 42'$. These measurements have been confirmed by Marignac.

Acid oxalate of potassium is used as a weak acid for scouring metals; also for removing ink-stains and iron-mould, the double oxalate of iron and potassium being soluble in water.

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* In De la Provostaye's measurements, the primary form is a pyramid with its axis seven times as long as in those of Rammelsberg.

† The faces here denoted by $[\infty P\infty]$ and $+2P2$ were regarded by Rammelsberg as belonging to a rhombic prism.

*Hyperacid salt. Tetroxalate* or *Quadroxalate of Potassium*, $C^4H^3KO^8.2H^2O$ or $C^2HKO^4.C^2H^2O^4.2H^2O$.—This salt discovered by Savary and Wiegleb, and analysed by Wollaston (Phil. Trans. 1808, p. 99), is prepared by saturating 1 pt. of oxalic acid with carbonate of potassium, adding 3 pts. of oxalic acid and leaving the solution to crystallise. A solution of equal parts of oxalic acid and chloride of potassium also deposits this salt in crystals on cooling. (Anderson, Chem. Soc. Qu. J. i. 231.)

Hyperacid oxalate of potassium crystallises in beautiful triclinic prisms, sometimes of large dimensions. Dominant combination ∞,'P . ∞P̄∞ . ∞P,' . ∞P̆∞ . 2,P,∞ . oP . 2,P'∞, with the secondary faces 4,P,∞, 4,P'∞, P', 'P, ¼P', P¼, ∞,'P⅓, P. Axes *a* : *b* : *c* = 2·10044 : 3·2555 : 1, the axis *a* being supposed vertical, *b* directed from left to right, *c* towards the observer. Angles of the axes α = 96° 12′; β = 79° 29′; γ = 97° 5′. Inclinations of faces oP : ∞P,' = 82° 30′; ∞P̆∞ ∞P,' = 111° 20′; P,' : ∞,'P = 146° 33′; oP : 2,P'∞ = 144° 30′; 2'P,∞ : ∞P∞ = 119° 25′; oP : 2,P'∞ = 148° 10′; 2,P'∞ : ∞P̄∞ = 127° 55′ (De la Provostaye, *loc. cit.* The measurements have been confirmed by Rammelsberg). The crystals dissolve in 20·17 pts. water at 20° and give off their water of crystallisation at 128°.

According to Bérard, this salt is sometimes met with in commerce as salt of sorrel, according to Gmelin, when the latter is prepared by half neutralising oxalic acid with carbonate of potassium.

OXALATES OF RUBIDIUM. The *neutral salt*, $C^2Rb^2O^4.H^2O$, crystallises by slow evaporation of a cold saturated solution, in irregular imperfectly developed monoclinic crystals isomorphous with those of the neutral potassium-salt and exhibiting the combination P . ∞P∞ . + P∞ . oP. The inclinations of the faces are approximately + P : + P (clin.) = 73°; − P : + P (basal) = 122 to 113½°; ∞P∞ : − P = 129° to 130°. (Piccard, J. pr. Chem. lxxxvi. 449.)

The *acid salt*, $C^2HRbO^4$, forms small monoclinic crystals, isomorphous with the acid potassium-salt, and generally exhibiting the combination ∞P . [∞P∞] . [P∞] . [2P∞] . oP. Approximately, ∞P : ∞P (clin.) = 152° 30′; [P∞] : [P∞], in the same = 122°; [2P∞] : [∞P∞] = 137° 45′. The prismatic faces are vertically striated. (Piccard.)

The *hyperacid salt*, $C^4H^3RbO^4$, is obtained in large crystals by dissolving the acid salt in dilute nitric acid, and leaving the solution to evaporate. (Grandeau, Ann. Ch. Phys. [3] lxvii. 155.)

OXALATE OF SILVER. $C^2Ag^2O^4$.—Obtained pure and anhydrous as a white crystalline precipitate, by adding oxalic acid to nitrate of silver. It is very sparingly soluble in cold, somewhat more in hot water, perfectly insoluble in alcohol and ether. It dissolves readily in ammonia and carbonate of ammonia; the solution turns brown when exposed to light, and when slowly evaporated in the dark, yields the oxalate of silver in large, hard, shining prisms. It decomposes between 110° and 150°, and detonates when suddenly heated. With *iodide of methylene*, oxalate of silver yields dioxymethylene, $C^2H^4O^2$, together with iodide of silver and a mixture of carbonic anhydride and carbonic oxide (Butlerow, iii. 1006).—With *chloride of benzylene*, $C^7H^6Cl^2$, it yields by a similar reaction, bitter almond oil:

$$C^7H^6Cl^2 \quad + \quad C^2Ag^2O^4 \quad = \quad C^7H^6O \quad + \quad 2AgCl \quad + \quad CO^2 \quad + \quad O.$$

With *iodide of ethylene*, on the contrary, it yields nothing but iodide of silver and a mixture of carbonic anhydride and carbonic oxide:

$$C^2H^4I^2 \quad + \quad C^2Ag^2O^4 \quad = \quad 2AgI \quad + \quad CO^2 \quad + \quad CO.$$

Similarly with *bromide of amylene*. (Golowkinsky, Ann. Ch. Pharm. cxi. 252.)

*Ammonio-oxalate of Silver*, $4NH^3.C^2Ag^2O^4 = \left.\begin{matrix}(C^2O^2)''\\ Ag^2\\ H^{12}\end{matrix}\right\}\begin{matrix}N^4\\ O^2,\end{matrix}$ is obtained as a spongy tumefied mass by passing dry ammonia-gas over dry oxalate of silver. It is easily soluble, has an alkaline reaction, and is decomposed by acids with separation of oxalate of silver. (Souchay and Lenssen.)

OXALATES OF SODIUM. The *neutral salt*, $C^2Na^2O^4$, occurs in a great number of plants, and is found in varech, by the incineration of which carbonate of sodium is obtained. It is anhydrous and difficult to obtain in regular crystals. 1 pt. of it dissolves in 26·78 pts. water at 21·8°, and in 16 pts. of boiling water (Pohl); in 36·4 pts. water at ordinary temperatures and 24·6 pts. boiling water. (Rammelsberg.)

The *acid oxalate*, $C^2HNaO^4.H^2O$, forms crystals which redden litmus.

*Sodio-potassic oxalate* has not been obtained. A boiling solution of salt of sorrel neutralised with carbonate of sodium yields on cooling or evaporation nothing but neutral oxalate of sodium. (Rammelsberg.)

OXALATES OF STRONTIUM. The neutral salt, $C^2Sr''O^4.H^2O$, obtained by precipitating a strontium-salt with a neutral alkaline oxalate, is a white powder soluble in 19·20 pts. of boiling water, sparingly soluble in cold, easily in hot solutions of chloride or nitrate of ammonium; retains its water of crystallisation at 100°. Wicke (Ann. Ch. Pharm. xc. 108), by precipitating nitrate of strontium with oxalic acid, obtained a salt in microscopic square-based octahedrons containing $C^2Sr''O^4.3H^2O$.

*Acid salt.*—Clapton (Chem. Soc. J. vi. 123), by mixing concentrated solutions of oxalic acid and chloride of strontium, obtained crystals intermediate in composition between the neutral and acid oxalates of strontium. Souchay and Lenssen once obtained a salt containing $C^2Sr''O^4.C^2H^2O^4.2H^2O$ or $C^4H^2Sr''O^8.2H^2O$, by mixing a rather strong solution of chloride of strontium with 1 or 2 measures of strong hydrochloric acid, and 3 or 4 measures of solution of oxalic acid saturated at 60°. After standing for some days at 0°, the liquid deposited, together with oxalic acid and the neutral salt, crusts of an acid salt, consisting of highly lustrous prismatic crystals with pyramidal summits, mostly united in geodes. These crystals effloresced in the air, and were resolved by water into free oxalic acid and the neutral salt. They gave by analysis 34·0 per cent. strontia, the formula requiring 34·4 per cent.

**OXALATE OF TANTALUM?** Oxalic acid dissolves only a trace of tantalic oxide, but salt of sorrel dissolves it in considerable quantity, forming a colourless solution from which alkalis throw down tantalic oxide. (Berzelius.)

**OXALATE OF TELLURIUM?** Oxalic acid dissolves telluric hydrate, and the solution yields radiate crystalline grains which dissolve easily and without decomposition in water. (Berzelius.)

**OXALATES OF THALLIUM.** The *neutral salt*, $C^2Tl^2O^4$, is prepared by boiling together equivalent quantities of thallic carbonate and oxalic acid in just sufficient water to dissolve the product while hot. On cooling, the oxalate crystallises in small white lustrous prisms (Crookes, Chem. Soc. J. xvii. 150); in small nearly right-angled four-sided laminæ (Kuhlmann, Compt. rend. lv. 607). It dissolves in 69·3 pts. water, at 15·5° and in 11 pts. boiling water; insoluble in alcohol. Hydrochloric acid converts it into a spongy mass of chloride of thallium. It may be heated to 271° without appreciable loss of weight; but decomposes at a red heat, leaving a mixture of oxide and metallic thallium. (Crookes.)

The *acid salt*, $C^2HTlO^4.H^2O$, crystallises in large pearly plates which are slightly efflorescent and give off their water at 138°. Dissolves in 18·7 pts. water at 15·5° and in less than its own bulk of boiling water, forming a syrupy solution. It is strongly acid to test-paper. (Crookes.)

**OXALATE OF THORINUM.** $C^2Th''O^4.H^2O$.—Heavy white precipitate insoluble in water, very slightly soluble in oxalic acid or in dilute mineral acids. (Berzelius. Chydenius, Pogg. Ann. cxix. 43.)

*Potassio-thorinic oxalate.* White precipitate insoluble in water and in aqueous oxalic acid. Turns black when ignited, and then, if in contact with the air, leaves a white mixture of thorina and carbonate of potassium. (Berzelius.)

**OXALATES OF TIN.** *a. Stannous salts.*—The salt $C^2Sn O^4$ is obtained easily and in large quantity by pouring a solution of tin in acetic acid into boiling aqueous oxalic acid. The stannous oxalate being nearly insoluble, separates immediately in shining neutral anhydrous needles resembling artificially crystallised calcic sulphate. It is insoluble in cold water, and is partially decomposed by boiling water, with production of a white salt (Hausmann and Löwenthal, Ann. Ch. Pharm. lxxix, 104). This salt treated with warm caustic ammonia yields white stannous hydrate, but with a somewhat concentrated solution of caustic potash, it yields anhydrous stannous oxide. Hydrochloric acid at the boiling heat dissolves an almost unlimited quantity of stannous oxalate; and, as the solution cools, the whole of the oxalic acid is deposited in crystals, while stannous chloride remains in solution; but if a little water be added to the solution, stannous oxalate crystallises out. (R. Böttger, J. pr. Chem. lxxvi. 238.)

Stannous oxalate dissolves in the oxalates of ammonium, potassium, and sodium, forming double salts.

*Ammonio-stannous oxalate*, $C^4Sn''(NH^4)^2O^8.H^2O$, is obtained by dissolving stannous oxalate in a boiling concentrated solution of oxalate of ammonium, and mixing the solution when cold with alcohol. It then, after some time, deposits the double salt in stellate groups of needles which effloresce in the air, are insoluble in alcohol, and have a very sweet taste. The concentrated solution, when left to itself for some time, deposits stannous oxalate (Hausmann and Löwenthal). This salt is isomorphous with the potassium-salt (*inf.*); it fuses and detonates when heated. (Bouquet, Ann. Ch. Pharm. lxiv. 278.)

*Potassio-stannous oxalate.* Obtained: 1. By dissolving recently precipitated stannous oxalate in a hot concentrated solution of neutral oxalate of potassium; purified by recrystallisation (Hausmann and Löwenthal).—2. By treating acid oxalate of potassium with a large excess of stannous oxide (Bouquet).—Transparent, colourless prismatic crystals which dissolve readily in hot water, less readily in cold water, and are insoluble in alcohol (Hausmann and Löwenthal).—Bouquet's salt forms large colourless crystals, which dissolve readily in cold water, forming a solution which becomes milky after a while, and decomposes quickly when boiled, yielding first a white gelatinous and afterwards a black precipitate.—The salt has a strong sweet taste, but leaves a bitter after-taste. It reddens litmus, and is not decomposed when heated at 100° in contact with the air. (Hausmann and Löwenthal.)

*Sodio-stannous oxalate.* Prepared like the potassium salt which it resembles (H. and L.). Anhydrous and crystallisable (Bouquet.)

*β. Stannic salt.* Recently prepared stannic oxide (obtained by precipitating a solution of stannic chloride with sulphate of sodium) dissolves readily in warm oxalic acid, and a nearly saturated solution yields by evaporation white shining laminæ containing variable quantities of stannic oxide, and becoming by repeated crystallisation continually poorer in that substance, till at length pure oxalic acid crystallises out. The same solution yields, with sulphuric, nitric or hydrochloric acid—also with alkalis, alkaline carbonates, chlorides, nitrates, sulphates, &c.—white precipitates soluble in water and containing $12SnO^2.C^4O^6.12H^2O$. The precipitate formed by the fixed alkalis or their carbonates becomes insoluble in water, when left in contact with it for some time or heated with it. (Hausmann and Löwenthal.)

OXALATE OF TITANIUM. Precipitated in the form of a curdy mass, on boiling an aqueous solution of a titanic salt mixed with oxalic acid (Laugier). Any ferric oxide that may be contained in the liquid remains in it for the most part. The dried precipitate imparts to moist litmus-paper a red tint, which nearly disappears on drying. The precipitate is soluble in excess, both of aqueous oxalic acid and of hydrochlorate of titanium. Contains $12TiO^2.C^4TiO^8.12H^2O$. (H. Rose.)

OXALATES OF URANIUM. *a. Uranous salts.*—Uranous oxalate, $C^2U''O^4.3H^2O$, is a greenish-white precipitate obtained by mixing a solution of uranous chloride with oxalic acid; gives off 2 at. water in vacuo.

*Ammonio-uranous oxalate.* $C^4(NH^4)^2U''O^8$ is obtained in crystals by boiling recently precipitated uranous hydrate in a solution of acid oxalate of ammonium (Rammelsberg).—*Potassio-uranous oxalate* obtained in a similar manner is a grey powder.

*β. Uranic salts. Uranic oxalate* or *Oxalate of Uranyl*, $C^2(U^2O^2)''O^4.3H^2O$, is deposited in crystalline grains on mixing a warm concentrated solution of uranic nitrate with oxalic acid, and leaving the solution to cool. The air-dried salt heated to 100°—120° gives off nearly 9 per cent. (2 at.) water, which it takes up again on exposure to the air; at 300° the mono-hydrated salt turns brown and is converted almost instantly, with evolution of water and carbonic anhydride, into a copper-coloured powder of uranous oxide, which by ignition in the air is converted into green uranoso-uranic oxide: $C^2(U^2O^2)''O^4 = 2UO + 2CO^2$. (Ebelmen, Ann. Ch. Phys. [3] v. 189.)

Uranic oxalate is nearly insoluble in cold water, dissolves in 30 pts. of boiling water, is more soluble in acids, and dissolves easily in the oxalates of ammonium and potassium, forming double salts which crystallise on cooling.

*Ammonio-uranic oxalate*, $C^4(NH^4)^2(U^2O^2)''O^8.4H^2O$, is obtained in fine transparent yellow crystals by dissolving uranic oxalate in warm aqueous ammonia (Péligot). The crystals are trimetric prisms, exhibiting the combination $\bar{P}\infty . \infty\breve{P}\infty . \infty\breve{P}2 . \infty P . \infty\bar{P}\infty$. Axes $a : b : c = 0{\cdot}6686 : 1 : 0{\cdot}5941$. Angle $\breve{P}\infty : \breve{P}\infty = 112° 28' : \infty\breve{P}\infty : \infty\bar{P}2 = 139° 55' : \infty\breve{P}2 : \infty P = 160° 45' : \bar{P}\infty : \infty\breve{P}2 = 115° 15'; \breve{P}\infty : \infty P = 106° 30'$.

*Potassio-uranic oxalate*, $C^4K^2(U^2O^2)''O^8.3H^2O$, forms monoclinic prisms permanent in the air and giving off all their water of crystallisation at 100°. Dominant faces $\infty P$, $\infty P\infty$, $oP$. Angle $\infty P : \infty P = 131° 2'$; $\infty P : \infty P\infty = 114° 20'$; $\infty P : oP = 111° 28'$. (Ebelmen.)

OXALATES OF VANADIUM.—*Vanadic oxalate.*—Aqueous oxalic acid saturated with hydrated vanadic oxide yields on evaporation a light blue, translucent gum, which dissolves slowly in cold water, more quickly in hot water. The aqueous solution mixed with a large quantity of oxalic acid yields by spontaneous evaporation blue crystals readily soluble in water. (Berzelius, Pogg. Ann. xxii. 33.)

*Potassio-vanadic oxalate.* Salt of sorrel saturated with hydrated vanadic oxide dries up to a dark blue, amorphous varnish, which dissolves slowly in water. (Berzelius.)

*Oxalo-vanadic acid.* When vanadic oxalate is evaporated with nitric acid, and the residue treated with water, the greater part dissolves, forming a yellowish-red solution, which on evaporation leaves oxalo-vanadic acid in the form of a reddish-yellow, amorphous extract, likewise soluble in water. An excess of oxalic acid immediately reduces the vanadic acid to vanadic oxide. (Berzelius.)

OXALATE OF YTTRIUM, $C^2Y''O^4.3H^2O$.—White precipitate, bulky and curdy at first, but shrinking together after a while; insoluble in water, aqueous oxalic and dilute hydrochloric acid, but soluble in nitric and in strong hydrochloric acid (Berlin).

This description applies strictly, not to pure oxalate of yttrium, but to a mixture of the oxalates of yttrium, erbium, and terbium; the pure yttrium-salt is more soluble in acids than the oxalates of erbium and terbium, a property which affords the means of separating yttria from erbia and terbia. (Mosander.)

*Oxalate of yttrium and potassium*, $C^4K^2Y''O^8$, is a heavy white precipitate, insoluble in water.

**Oxalate of Zinc.** $C^2Zn''O^4.2H^2O$.—White precipitate, insoluble in water, soluble in hydrochloric acid and in ammonia, also in a warm solution of sal-ammoniac.

*Oxalate of zinc and ammonium.*—*a.* Deposited in needles when oxalic acid is added to an aqueous solution of chloride of zinc supersaturated with ammonia. (Wackenroder, Ann. Ch. Pharm. x. 63.)

*β.* When an aqueous solution of acid oxalate of ammonium is digested with carbonate of zinc till it is completely saturated, oxalate of zinc separates out, and the filtrate when evaporated leaves milk-white nodules, containing $C^6(NH^4)^4Zn''O^{12}.3H^2O$, which slowly effloresce and give off water, are nearly insoluble in cold water, but are decomposed by hot water, with separation of carbonate of zinc. (Kayser, Pogg. Ann. lx. 140.)

*Oxalate of zinc and potassium.* $C^4K^2Zn''O^8.4H^2O$.—A concentrated solution of normal oxalate of potassium boiled for some time with oxalate of zinc, and then filtered, yields, on cooling, small transparent efflorescent tables, nearly insoluble in cold water, and decomposed by boiling water, with separation of oxalate of zinc. (Kayser.)

**Oxalate of Zirconium.**—Oxalic acid and oxalate of ammonium added to solutions of zirconium-salts, throw down a white opaline flaky precipitate, insoluble in water and in boiling aqueous oxalic acid. (Dubois and Silveira.)

**OXALIC ACID, AMIDES OF.** Oxalic acid, like other dibasic acids of the series $C^nH^{2n-2}O^4$, should yield four normal amides by elimination of water from its acid and neutral ammonium-salts, thus:

$$\underset{\text{Acid ammonium-salt.}}{C^2H(NH^4)O^4} - H^2O = \underbrace{C^2H^3NO^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}}_{\text{Oxamic acid.}}$$

$$\underset{\text{Acid ammonium-salt.}}{C^2H(NH^4)O^4} - 2H^2O = \underbrace{C^2HNO^2 = \left.\begin{matrix}(C^2O^2)''\\H\end{matrix}\right\}N.}_{\text{Oximide (unknown).}}$$

$$\underset{\text{Neutral ammonium-salt.}}{C^2(NH^4)^2O^4} - 2H^2O = \underbrace{C^2H^4N^2O^2 = \left.\begin{matrix}(C^2O^2)''\\H^4\end{matrix}\right\}N^2}_{\text{Oxamide.}}$$

$$\underset{\text{Neutral ammonium-salt.}}{C^2(NH^4)^2O^4} - 4H^2O = \underset{\text{Oxanitrile (Cyanogen).}}{C^2N^2.}$$

The hydrogen in oxamic acid and oxamide may be more or less replaced by alcohol-radicles, thus giving rise to alkalamides, *e.g.* Methyl-oxamic acid, $C^2H^2(CH^3)NO^3$; diethyloxamide, $C^2H^2(C^2H^5)^2N^2O^2$, &c. (See Oxamic Ethers and Oxamide.)

There is also a number of other bodies, chiefly derivatives of uric acid, which may be regarded, with respect to their constitution and transformation, but not to their mode of formation, as amides of oxalic acid of a more complex character, namely as deriving from two or more molecules of oxalic acid by addition of ammonia and abstraction of water, *e.g.*

$$2C^2H^2O^4 + 2NH^3 - 4H^2O = C^4H^2N^2O^4 = \underset{\text{Dioxalylamide or Alloxan.}}{\left.\begin{matrix}(C^2O^2)''\\(C^2O^2)''\\H^2\end{matrix}\right\}N^2}$$

$$2C^2H^2O^4 + 2NH^3 - 3H^2O = C^4H^4N^2O^5 = \underset{\text{Dioxalylamic acid or Alloxanic acid.}}{\left.\begin{matrix}(C^2O^2)''\\(C^2O^2)''\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}}$$

Other compounds of the same family may be derived in a similar manner from a molecule of oxalic acid and a molecule of another acid, thus:

$$\begin{array}{llllll}
C^2H^2O^4 & + CO^2 & + 2NH^3 & - 3H^2O & = & C^3H^2N^2O^3 \text{ Parabanic acid.}\\
\underset{\text{Oxalic acid.}}{C^2H^2O^4} & + \underset{\text{Carbonic anhydride.}}{CO^2} & + 2NH^3 & - 2H^2O & = & C^3H^4N^2O^4 \text{ Oxaluric acid.}
\end{array}$$

$$\begin{array}{llllll}
C^2H^2O^4 & + CH^2O^2 & + 2NH^3 & - 3H^2O & = & C^3H^4N^2O^3 \text{ Parabanic acid.}\\
\underset{\text{Oxalic acid.}}{2C^2H^2O^4} & + \underset{\text{Formic acid.}}{CH^2O^2} & + 4NH^3 & - 7H^2O & = & C^5H^4N^4O^3 \text{ Uric acid.}
\end{array}$$

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$$\begin{array}{lllllllllll}
C^2H^2O^4 & + & CH^2O^2 & + & CO^2 & + & 4NH^3 & - & 5H^2O & = & C^4H^6N^4O^3 \text{ Allantoïn.}\\
2C^2H^2O^4 & + & CH^2O^2 & + & CO^2 & + & 4NH^3 & - & 7H^2O & = & C^6H^4N^4O^5 \text{ Oxalantin.}\\
\text{Oxalic acid.} & & \text{Formic acid.} & & \text{Carbonic anhydride.} & & & & & &
\end{array}$$

$$\begin{array}{lllllllll}
C^2H^2O^4 & + & C^2H^2O^3 & + & 2NH^3 & - & 3H^2O & = & C^4H^4N^2O^4 \text{ Dialuric acid.}\\
3C^2H^2O^4 & + & C^2H^2O^3 & + & 4NH^3 & - & 8H^2O & = & C^8H^4N^4O^7 \text{ Alloxantin.}\\
\text{Oxalic acid.} & & \text{Glyoxalic acid.} & & & & & &
\end{array}$$

$$\begin{array}{lllllllllll}
C^2H^2O^4 & + & C^2H^2O^3 & + & CO^2 & + & 4NH^3 & - & 6H^2O & = & C^5H^4N^4O^3 \text{ Uric acid}\\
C^2H^2O^4 & + & C^2H^2O^3 & + & CO^2 & + & 4NH^3 & - & 5H^2O & = & C^5H^6N^4O^4 \text{ Pseudo-uric acid.}\\
\text{Oxalic acid.} & & \text{Glyoxalic acid.} & & \text{Carbonic anhydride.} & & & & & &
\end{array}$$

All these compounds have been or will be described in their alphabetical places. See also URIC ACID, DERIVATIVES OF.

**OXALIC ETHERS.** Oxalic acid forms with monatomic alcohol-radicles two series of ethers, analogous to the neutral and acid metallic oxalates. Only those of methyl, ethyl, amyl and allyl have however been yet obtained.

The neutral ethers of the monatomic alcohol-radicles are produced by the action of dehydrated oxalic acid on the corresponding alcohols, or by distilling the alcohols with sulphuric acid and oxalic acid or an oxalate; or by passing hydrochloric acid gas into a solution of oxalic acid in the alcohol. They are volatile without decomposition in the dry state, but in presence of water, bases, or acids, they are easily resolved into oxalic acid and an alcohol. Sulphuric acid decomposes them, with elimination of carbonic oxide and production of carbonic, or under certain conditions, of formic ethers. With ammonia they yield either oxamide or ethers of oxamic acid. When treated with the zinc-compounds of the alcohol-radicles and afterwards with water, they yield ethers of the lactic or glycollic series. With chlorine they yield chlorinated ethers.

The acid ethers of oxalic acid have not been so fully examined as the neutral ethers, only those of ethyl and amyl being known. They are obtained as bye-products in the preparation of the neutral ethers; ethyl-oxalic acid also by the action of alcoholic potash on neutral ethylic oxalate.

An oxalate of the diatomic radicle ethylene appears to be produced by the action of bromide of ethylene on oxalate of silver.

**Oxalate of Allyl,** $C^8H^{10}O^4 = C^2(C^3H^5)^2O^4$.—Produced by digesting oxalate of silver with allylic iodide and anhydrous ether at 100°, and rectifying. It is an oily liquid, smelling like oxalate of ethyl, with a slight admixture of the odour of mustard-oil. Specific gravity 1·055 at 15°. Boiling point 206°—207°. (Hofmann and Cahours.)

**Oxalates of Amyl.** *a.* NEUTRAL AMYLIC OXALATE, $C^{12}H^{22}O^4 = C^2(C^5H^{11})^2O^4$. (Balard, Ann. Ch. Phys. [3] xii. 311.)—When potato fusel-oil or pure amylic alcohol is treated with a large excess of crystallised oxalic acid, two liquids are formed, the lower being watery and consisting of a saturated aqueous solution of oxalic acid, while the upper is oily, has a strong odour of bugs, and deposits oxalic acid on cooling. On distilling this oily liquid, the temperature gradually rises, and amylic oxalate distils over. It may be purified by redistillation.

Amylic oxalate is an oily liquid having a very decided odour of bugs. It boils at 262°. Vapour density 8·4. It is decomposed by *water* and more quickly by aqueous *alkalis*, yielding amylic alcohol and an oxalate. By *aqueous ammonia* it is converted into amylic alcohol and oxamide; by *gaseous* or *alcoholic ammonia* into amylic alcohol and amylic oxamate. Treated with *zinc-ethyl* and then with *water*, it yields amylic diethoxalate or amylic leucate (see page 274). On account of its high boiling point, it may be used for the preparation of other amylic ethers by double decomposition.

Chancel has obtained *methyl-amylic oxalate* and *ethyl-amylic oxalate* by processes similar to that which yields the oxalate of methyl and ethyl (p. 271).

AMYLOXALIC ACID, $C^7H^{12}O^4 = C^2(C^5H^{11})HO^4$. *Oxalamylic acid. Acid oxalate of amyl* (Balard, Ann. Ch. Phys. [3] xii. 309).—The oily liquid obtained as above by heating amylic alcohol with oxalic acid yields, when saturated with chalk, a solution of amyloxalate of calcium which crystallises on cooling. This salt serves for the preparation of the other amyloxalates.

Amyloxalic acid is an oily liquid having an odour of bugs. By dry distillation it yields neutral oxalate of amyl, carbonic oxide and carbonic anhydride:

$$2C^2(C^5H^{11})HO^4 = C^2(C^5H^{11})^2O^4 + CO + CO^2 + H^2O.$$

The *amyloxalates* are very unstable, their solutions when boiled reproducing amylic alcohol.

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The *potassium-salt* forms beautiful nacreous laminæ, greasy to the touch.—The *calcium-salt*, $C^{14}H^{22}Ca''O^8.2H^2O$, crystallises in beautiful crystalline scales, more soluble in cold than in hot water. Exposed to a current of dry air at 100°, it decomposes yielding amylic alcohol. The *silver-salt*, $C^7H^{11}AgO^4$, forms anhydrous scales having a nacreous lustre, sparingly soluble, and very greasy to the touch. It gradually alters, even when dry, especially if exposed to light.

**Oxalates of Ethyl.** *a.* NEUTRAL ETHYLIC OXALATE, $C^6H^{10}O^4 = \left.\begin{matrix}(C^2O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2$.

*Oxalic ether.*—This compound was discovered by Bergmann (*Opuscula*, i. 256) and has been more particularly investigated by Thénard (Mém. d' Arcueil, ii. 11), Bauhof (Schw. J. xix. 308), Dumas and Boullay (J. Pharm. xiv. 113), Dumas (Ann. Ch. Phys. liv. 227), Löwig (J. pr. Chem. lxxxiii. 129), and Frankland and Duppa (p. 272).

*Formation.*—1. By heating alcohol with oxalic acid, more readily in presence of sulphuric or hydrochloric acid.—2. Together with chlorethylic formate and hydrochloric acid, in the decomposition of perchloromethylic oxalate (p. 272) by alcohol, (Cahours, Ann. Ch. Phys. [2] xix. 348).—3. In the preparation of crude aldehyde by distilling a mixture of equal parts of manganic peroxide, sulphuric acid, and spirit of 20 per cent. (C. Schmidt, Ann. Ch. Pharm. lxxxiii. 330.)

*Preparation.*—1. One part of acid potassic oxalate (salt of sorrel) is mixed with 1 pt. alcohol and 2 pts. strong sulphuric acid; the mixture is distilled; water is added as soon as the distillate begins to show turbidity, the receiver then changed, and the distillation continued without cooling. On mixing the distillate with water, the oxalic ether separates and falls to the bottom; the water is then removed with a pipette, and the ether washed and rectified. (Dumas and Boullay.)

2. A more expeditious and productive method is to heat dehydrated oxalic acid with alcohol. Mitscherlich heats 1 pt. of effloresced oxalic acid with 6 pts. absolute alcohol, distils till the temperature of the liquid in the retort rises to 140°, then pours back the alcohol which has passed over, and distils till the thermometer rises to 165°; the remaining liquid, consisting chiefly of oxalic ether, is repeatedly shaken with water and rectified over oxide of lead.—According to Löwig, a much smaller quantity of alcohol is sufficient for the purpose. He pours $1\frac{3}{4}$lb. of absolute alcohol, or spirit of 97 or 98 per cent., on $1\frac{3}{8}$lb. of dehydrated oxalic acid; distils slowly till the thermometer rises to 130°, and then distils the product quickly off. The distillate thus obtained consists of oxalic ether, with a considerable quantity of formic and a small quantity of carbonic ether. 2800 grms. of dehydrated oxalic acid thus treated yield 1800 grms. oxalic ether and 600 grms. formic ether. An additional quantity of oxalic and formic ether may be separated from the distillate which goes over below 120°, by neutralising with carbonate of potassium. These ethers may be separated by fractional distillation, the formic ether passing over between 55° and 75°, the oxalic ether at about 185°.—According to Kekulé (*Lehrbuch*, ii. 15) the best mode of preparation is to dissolve dehydrated oxalic acid in not more than twice its weight of absolute alcohol, saturate with dry hydrochloric acid gas, precipitate the ether with water after the liquid has stood for several hours, wash it several times with water, dry over chloride of calcium, and rectify.

Considerable quantities of oxalic ether are obtained by merely leaving oxalic acid in contact with absolute alcohol for a few weeks, best at 40°—50°. (Liebig, Ann. Ch. Pharm. lxv. 350.)

*Properties.*—Ethylic oxalate is a colourless oily liquid, having an aromatic odour, specific gravity = 1·0929 at 7·5° (Dumas and Boullay); 1·0824 at 15°, Mendelejef (Pogg. Ann. cxl. 229). Boiling point 183°—184° (Dumas and Boullay), 186° (Kekulé). Vapour-density, obs. = 5·087 (Dumas and Boullay), 5·10 (Cahours), calc. = 5·06. It is very slightly soluble in *water*, but dissolves easily in *alcohol*.

*Decompositions.*—1. Ethylic oxalate is decomposed by contact with *water*, yielding alcohol and oxalic acid. Boiled with aqueous *potash* or *soda*, it is quickly converted into alcohol and an oxalate of the alkali-metal.—2. Its alcoholic solution mixed with *alcoholic potash* yields alcohol and a precipitate of ethyl-oxalate of potassium:

$$C^2(C^2H^5)^2O^4 \quad + \quad KHO \quad = \quad C^2(C^2H^5)KO^4 \quad + \quad C^2H^5.H.O.$$

3. *Ammonia-gas* decomposes it into alcohol and ethylic oxamate (oxamethane):

$$\underset{\text{Ethylic oxalate.}}{\left.\begin{matrix}(C^2O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2} \quad + \quad NH^3 \quad = \quad \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O} \quad + \quad \underset{\text{Ethylic oxamate.}}{\left.\begin{matrix}H^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}}$$

4. With *aqueous ammonia* it yields alcohol and oxamide:

$$\left.\begin{matrix}(C^2O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2 \quad + \quad 2NH^3 \quad = \quad 2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) \quad + \quad \left.\begin{matrix}(C^2O^2)''\\H^4\end{matrix}\right\}N^2$$

5. With *ethylamine*, in like manner, it yields diethyl-oxamide $(C^2O^2)''(C^2H^5)^2H^2N^2$; and with *diethylamine*, ethylic diethyloxamate

$\left.\begin{matrix}(C^2H^5)^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$; while *triethylamine* does not act upon it. On these reactions Hofmann has founded an easy method of separating the bases produced by heating ethylic iodide with ammonia (ii. 555). Similarly with the *methylamines* (iii. 998).

6. Ethylic oxalate is converting by *potassium* or *sodium* into ethylic carbonate, with evolution of carbonic oxide: $C^2(C^2H^5)^2O^4 \;=\; C(C^2H^5)^2O^3 + CO$; the reaction is complicated however by the formation of several other products, amongst which is a black substance called by Löwig and Weidmann, *nigric acid* (see *Gmelin's Handbook*, ix. 181).

7. When ethylic oxalate is agitated with *sodium-amalgam* in a vessel externally cooled, a product is obtained which is separated by ether into a soluble and an insoluble portion, the latter consisting of fermentable sugar together with sodic oxalate and at least one other sodium-salt, while the ethereal solution yields by spontaneous evaporation, crystals having the composition $C^{11}H^{16}O^8$, and consisting of the ethylic ether of a tribasic acid $C^5H^6O^8$, called desoxalic acid, because it is produced by deoxidation of oxalic acid: $5C^2H^2O^4 + 5H^2 = 2C^5H^6O^8 + 4H^2O$, and racemo-carbonic acid, because it contains the elements of racemic acid, $C^4H^6O^6$, and carbonic anhydride, $CO^2$, and is resolved into those two compounds when its aqueous solution is heated in a sealed tube with a small quantity of sulphuric acid (Löwig). The decomposition of ethylic oxalate by sodium-amalgam has not been completely investigated, but the formation of racemo-carbonic acid and sugar may be represented by the equation:

$$\underset{\text{Oxalic acid.}}{8C^2H^2O^4} + 14H^2 = \underset{\substack{\text{Racemo-}\\\text{carbonic acid.}}}{2C^5H^6O^8} + \underset{\text{Glucose.}}{C^6H^{12}O^6} + 10H^2O.$$

(See Racemo-carbonic Acid.)

8. Ethylic oxalate treated with *zinc-ethyl* or with zinc and ethylic iodide (which produce zinc-ethyl) and afterwards with water, yields ethylic diethoxalate or leucic ether, $C^6H^{11}(C^2H^5)O^3$; and homologous products, in like manner, with *zinc-methyl* and *zinc-amyl*. (Frankland and Duppa, see page 272.)

*Combination.*—Ethylic oxalate unites with *stannic-chloride*, forming a crystalline compound $C^6H^{10}O^4.SnCl^4$.

***Perchlorethylic Oxalate***, $C^6Cl^{10}O^4$.—This compound, also called *Perchlorovinic oxalate*, *Chloroxalic ether*, and *Perchloroxalic ether*, was discovered and investigated by Malaguti (Ann. Ch. Phys. [2] lxxiv. 299). It is produced by the action of chlorine on oxalic ether in sunshine. It is colourless, crystallises in quadrangular laminæ, is destitute of taste and smell, perfectly neutral, transparent when newly prepared, but becomes opaque after some time. It melts at 144° with incipient decomposition. It is insoluble in *water*. When exposed for some time to *moist air*, it becomes acid, gives off fumes and ultimately liquefies. *Alcohol*, *wood-spirit*, *amyl-alcohol*, *oil of turpentine*, and *acetone* decompose it immediately; common *ether*, *acetic ether*, and several other ethers, less rapidly.

Dry *ammonia-gas* converts it into pentachlorinated ethylic oxamate, forming at the same time another amide (probably trichloracetamide, and one or two ammonium-salts). With *aqueous ammonia* it yields oxamide and trichloracetamide. The reactions with ammonia appear to take place as shown by the equations:

$$C^6Cl^{10}O^4 + 2NH^3 = \underset{\text{Chloroxamethane.}}{C^4H^2Cl^5NO^3} + \underset{\text{Trichloracetamide.}}{C^2H^2Cl^3NO} + 2HCl.$$

$$\underset{\text{Chloroxamethane.}}{C^4H^2Cl^5NO^3} + 2NH^3 = \underset{\text{Trichloracetamide.}}{C^2H^2Cl^3NO} + \underset{\text{Oxamide.}}{C^2H^4N^2O^2} + 2HCl.$$

With *alcohol* it yields a number of compounds among which are trichloracetic acid, hydrochloric acid, chloride of ethyl, and an oil called chloroxethide which Malaguti represents by the formula $C^8Cl^{10}O^{14}$ (p. 271). When *methylic alcohol* is dropped upon chloroxalic ether, hydrochloric acid is evolved, and on adding water after the mixture has cooled, an oily mixture of oxalate and chlorocarbonate of methyl is precipitated.

*Potash* converts chloroxalic ether into oxalate, trichloracetate, and chloride of potassium:

$$C^6Cl^{10}O^4 + 4H^2O = C^2H^2O^4 + 2C^2HCl^3O^2 + 4HCl.$$

Chloroxalic ether several times subjected to rapid *distillation* is converted into chloride of carbonyl (phosgene gas), oxide of carbon, and chloride of trichloracetyl:

$$C^6Cl^{10}O^4 = COCl^2 + CO + 2(C^2Cl^3O.Cl).$$

When kept in a closed vessel, it appears to undergo after a while the same changes as when heated.

*Ethyl-methylic oxalate*, $C^5H^8O^4 = C^2(CH^3)(C^2H^5)O^4$ (Chancel, Compt. Chim. 1850, pp. 373, 403).—Produced by the action of ethyl-sulphate of potassium on the methyl-oxalate, or of the methyl-sulphate on the ethyl-oxalate:

$$(CH^3)KSO^4 \quad + \quad C^2(C^2H^5)KO^4 \quad = \quad K^2SO^4 \quad + \quad C^2(CH^3)(C^2H^5)O^4.$$

It is a transparent colourless liquid having a faint aromatic odour. Specific gravity 1·27 at 12°. Boils between 160° and 170°, distilling without alteration. Vapour-density 4·677 (calc. for 2 vol. = 4·5508). It burns with a bright flame blue at the edges.

It does not dissolve in *water* without decomposition: cold water and damp air decompose it slowly; boiling water dissolves it completely, decomposing it however into methylic alcohol, ethylic alcohol, and oxalic acid. *Potash* decomposes it immediately without the aid of heat. *Ammonia* also decomposes it rapidly, forming a precipitate of oxamide.

ETHYLOXALIC ACID, $C^4H^6O^4 = C^2H(C^2H^5)O^4$. *Oxalovinic acid. Acid oxalate of ethyl* (Mitscherlich, Pogg. Ann. xxxiii. 332).—The potassium-salt of this acid is produced by adding to a solution of oxalic ether in absolute alcohol, a quantity of alcoholic potash less than sufficient to form oxalate of potassium; and on dissolving this salt in hydrated alcohol, carefully saturating with sulphuric acid and neutralising with carbonate of lead or barium, the ethyl-oxalate of lead or barium is obtained.

The acid itself is prepared by decomposing either of these salts with sulphuric acid; but it is very unstable and is decomposed by concentration into alcohol and oxalic acid.

The *potassium-salt*, $C^2(C^2H^5)KO^4$, forms crystalline scales which begin to decompose towards 100°.

*Pentachlorethyloxalic acid* or *Chloroxalovinic acid*, $C^4HCl^5O^4$ (Malaguti, Ann. Ch. Phys. [2] lxxiv. 308).—This compound is not produced by the action of chlorine on ethyl-oxalic acid, but 1. In the decomposition of perchloroxalic ether by alcohol (p. 270).—2. When chloroxethide is treated with cold aqueous solutions of the fixed alkalis.—3. When pentachlorinated oxamate of ethyl is treated with aqueous ammonia:

$$C^4NH^2Cl^5O^3 \quad + \quad H^2O \quad = \quad C^4(NH^4)Cl^5O^4.$$

It may be prepared by placing the last-mentioned compound in contact with aqueous ammonia till it is completely dissolved, and evaporating in vacuo, whereby crystallised chloroxalovinate of ammonium is obtained. This salt is dissolved in water; the solution mixed with carbonate of sodium and evaporated, first on a sand-bath, afterwards in vacuo over oil of vitriol; the chloroxalovinate of sodium is extracted from the residue by absolute alcohol; the soda precipitated from this solution by the exact quantity of sulphuric acid required; the liquid filtered; any excess of sulphuric acid that it may contain precipitated by baryta-water; the liquid filtered again; and the alcoholic solution of chloroxalovinic acid evaporated to the crystallising point, first over the water-bath, and then in vacuo.

It forms colourless needles, which melt at a gentle heat; has a burning taste, and forms a white spot on the tongue; if placed for a while on the back of the hand, it produces violent pain and a white spot surrounded with an inflamed ring. It dissolves in all proportions in *water* and deliquesces very quickly in the air. It dissolves also in *alcohol* and in *ether*.

The *ammonium-salt* is crystalline; may be fused without decomposing; tastes very bitter and pungent; has a faint acid reaction. When heated to the boiling point, it decomposes, without evolving ammonia, and gives off thick vapours smelling of acetic acid. It deliquesces and turns yellow in the air, but becomes white again when dried in vacuo.

Malaguti has described a substance which he calls *anhydrous chloroxalovinic acid* or *chloroxethide*, $C^8Cl^{10}O^7$, but which appears to be merely a liquid modification of the preceding. It is obtained, among other products, by the action of alcohol on *perchloroxalic ether* (p. 270). It is quite neutral when newly prepared, but quickly turns acid by contact with moist air. It boils at 200°, becoming coloured at the same time. It is insoluble in water, but soluble in alcohol and in ether. Ammonia converts it into chloroxamethane.

**Oxalate of Ethylene.** $C^4H^4O^4 = \left.\begin{matrix}(C^2O^2)''\\(C^2H^4)''\end{matrix}\right\}O^2$. *Oxalate of glycol.*—This compound appears to be produced by the action of bromide of ethylene on oxalate of silver. By exhausting the product with ether, treating the ethereal solution with slaked lime, and evaporating the filtrate, a liquid was obtained, having a peculiar sweet taste, insoluble in water, boiling with decomposition at a high temperature, and yielding oxamide when treated with ammonia. (Wurtz, Ann. Ch. Phys. [3] lv. 400.)

**Oxalates of Methyl.** NEUTRAL METHYLIC OXALATE, $C^4H^6O^4 = \left.\begin{matrix}(C^2O^2)''\\(CH^3)^2\end{matrix}\right\}O^2$

(**Dumas** and **Péligot**, Ann. Ch. Phys. [2] lviii. 44.—**Weidmann** and **Schweizer**, Pogg. Ann. lxiii. 602.—**Wöhler**, Ann. Ch. Pharm. lxxxi. 376).—This compound is obtained by distilling a mixture of equal parts of sulphuric acid, oxalic acid, and wood-spirit; or by drenching 1 pt. of salt-of-sorrel with 1 pt. wood-spirit and 1 pt. sulphuric acid, leaving the mixture to stand for some time, and then distilling. Towards the end of the distillation, methylic oxalate passes over nearly pure and crystallises in the neck of the retort. The liquid product which first passes over also yields crystallised methylic oxalate when left to evaporate.

Methylic oxalate crystallises in colourless rhombic tablets, melts at 51°, and boils at 161°. It is soluble in *water*, *alcohol*, and *ether*, but the aqueous solution quickly decomposes into oxalic acid and methylic alcohol. The same decomposition is produced still more quickly by caustic *potash* or *soda*. With *aqueous ammonia* it yields oxamide; with *gaseous ammonia*, methylic oxamate (oxamethylane); with *zinc-ethyl* it yields methylic diethoxalate and homologous compounds (*infra*).

*Chloromethylic oxalates* (**Malaguti**, Ann. Ch. Pharm. xxxii. 49).—Chlorine gas acts very slowly on fused methylic oxalate in diffused daylight, forming a liquid product which appears to be dichloromethylic oxalate, $C^4H^2Cl^4O^4 = C^2(CHCl^2)^2O^4$, inasmuch as it is immediately resolved by water into carbonic oxide, oxalic acid, and hydrochloric acid:

$$C^4H^2Cl^4O^4 \quad + \quad 2H^2O \quad = \quad 2CO \quad + \quad C^2H^2O^4 \quad + \quad 4HCl.$$

In sunshine, chlorine acts more strongly, producing nacreous laminæ of trichloromethylic oxalate, $C^2(CCl^3)^2O^4$, which smell of chloride of carbonyl (phosgene) and are resolved by heat into that compound and carbonic oxide:

$$C^4Cl^6O^4 \quad = \quad CO \quad + \quad 3COCl^2.$$

With *alcohol* they yield ethylic oxalate, ethylic chloroformate, and hydrochloric acid:

$$C^2(CCl^3)^2O^4 \quad + \quad 4C^2H^6O \quad = \quad C^2(C^2H^5)^2O^4 \quad + \quad 2CCl(C^2H^5)O^2 \quad + \quad 4HCl.$$

*Compounds produced by the action of Zinc-ethyl, &c., on the Oxalic ethers.*

When the oxalates of the alcohol-radicles are treated with zinc-methyl, zinc-ethyl, &c., ethers are produced, the acids of which may be regarded as oxalic acid $\left.\begin{matrix}(C^2O^2)'' \\ H^2\end{matrix}\right\}O^2$, in which 1 atom of oxygen is replaced by an equivalent quantity (2 at.) of an alcohol-radicle, or what comes to the same thing, as glycollic acid $\left.\begin{matrix}(C^2H^2O)'' \\ H^2\end{matrix}\right\}O^2$, in which 2 at. hydrogen belonging to the radicle glycollyl are replaced by 2 at. of an alcohol-radicle. thus:

| | | |
|---|---|---|
| Dimethoxalic or Dimethoglycollic acid . | $C^4H^8O^3$ | $= \left.\begin{matrix}[C^2(CH^3)^2O]'' \\ H^2\end{matrix}\right\}O^2$ |
| Ethomethoxalic or Ethomethoglycollic acid . | $C^5H^{10}O^3$ | $= \left.\begin{matrix}[C^2(C^2H^5)(CH^3)O]'' \\ H^2\end{matrix}\right\}O^2$ |
| Diethoxalic or Diethoglycollic acid . . | $C^6H^{12}O^3$ | $= \left.\begin{matrix}[C^2(C^2H^5)^2O]'' \\ H^2\end{matrix}\right\}O^2$ |
| Amhydroxalic or Amoglycollic acid . . | $C^7H^{14}O^3$ | $= \left.\begin{matrix}[C^2(C^5H^{11})HO]'' \\ H^2\end{matrix}\right\}O^2$ |
| Ethamoxalic or Ethamoglycollic acid . . | $C^9H^{18}O^3$ | $= \left.\begin{matrix}[C^2(C^5H^{11})(C^2H^5)O]'' \\ H^2\end{matrix}\right\}O^2$ |
| Diamoxalic or Diamoglycollic acid . . | $C^{12}H^{24}O^3$ | $= \left.\begin{matrix}[C^2(C^5H^{11})^2O]'' \\ H^2\end{matrix}\right\}O^2$ |

These acids are therefore homologues of glycollic acid,—also of lactic acid $C^3H^6O^3$, which may be formulated as methydroxalic or methoglycollic acid, $\left.\begin{matrix}[C^2(CH^3)HO]'' \\ H^2\end{matrix}\right\}O^2$. The first in the above list is isomeric or identical with butylactic, the second with valerolactic, the third with leucic acid. **Frankland** (Proc. Roy. Soc. xii. 396) obtained ethylic leucate or diethoxalate by the action of zinc-ethyl on ethylic oxalate, and the ethers of the other acids of the series have been obtained in like manner by **Frankland** and **Duppa** (Proc. Roy. Soc. xiii. 140; xiv. 17, 79, 83, 191).

The acids of the glycollic or lactic series $C^nH^{2n}O^3$ differ from those of the acrylic series $C^nH^{2n-2}O^2$ (i. 53), by 1 atom of water: *e.g.*

$$\underset{\text{Lactic acid.}}{C^3H^6O^3} \quad - \quad H^2O \quad = \quad \underset{\text{Acrylic acid.}}{C^3H^4O^2}$$

And it has lately been shown by **Frankland** and **Duppa** (Chem. Soc. J. xviii. 133), that by the action of trichloride of phosphorus, which abstracts the elements of water, the ethylic ethers of the glycollic or lactic series may be converted into the ethylic ethers of a series of acids isomeric with the natural acids of the acrylic series. As the ethers are of course included under the same general empirical formula as the acids themselves (each ether being formed from its corresponding acid by addition of $C^2H^4$) the reaction may be represented by the general equation:

$$3C^nH^{2n}O^3 + PCl^3 = 3C^nH^{2n-2}O^2 + PH^3O^3 + 3HCl$$

$$e.g.\ \underset{\text{Ethylic leucate.}}{3C^8H^{16}O^3} + PCl^3 = \underset{\text{Ethylic ethocrotonate.}}{3C^8H^{14}O^2} + \underset{\text{Phosphorous acid.}}{PH^3O^3} + 3HCl$$

The ethers thus obtained may be converted into potassium- or barium-salts, and these into the corresponding acids, in the usual way. In this manner have been obtained:

| | |
|---|---|
| Methacrylic acid, isomeric with Crotonic acid . . . | $C^4H^6O^2$ |
| Methocrotonic acid, isomeric with Angelic acid . . . | $C^5H^8O^2$ |
| Ethocrotonic acid, isomeric with Pyroterebic acid . . | $C^6H^{10}O^2$ |
| Ethometho-crotonic acid, isomeric with Damaluric acid . | $C^7H^{12}O^2$ |

[For further details respecting the relations of these two series of acids, also of the acids of the acrylic to those of the acetic series, see APPENDIX.]

We now proceed to describe the preparation and properties of the several acids of the glycollic series above mentioned.

**1. Diethoxalic, Diethoglycollic or Leucic Acid,** $C^6H^{12}O^3$.—Ethylic oxalate treated with zinc-ethyl and afterwards with water yields ethylic leucate together with alcohol and hydrate of zinc. The first result may be thus stated:

$$C^6H^{10}O^4 + Zn''(C^2H^5)^2 + 2H^2O = C^6H^{11}(C^2H^5)O^3 + C^2H^6O + Zn''H^2O^2.$$

The reaction however takes place by two stages: the first product is a solid resinous-looking mass consisting of zinc-monethyl-ethylic leucate, $C^{10}H^{20}ZnO^3$,—a compound derived from oxalic ether by the substitution of 2 at. ethyl for 1 at. oxygen, and of 1 at. zinc-monethyl, $ZnC^2H^5$, for 1 at. ethyl,—and this compound when treated with water is resolved into ethylic leucate, alcohol, and zinc-hydrate:

$$\underset{\text{Ethylic oxalate.}}{\left.\begin{matrix}C^2O^2\\(C^2H^5)^2\end{matrix}\right\}O^2} + \underset{\text{Zinc-ethyl.}}{2Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.} = \underset{\text{Zinc-monethyl-ethylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ZnC^2H^5\\C^2H^5\end{matrix}\right\}O^2} + \underset{\text{Zinc-ethylo-ethylate.}}{Zn''\left\{\begin{matrix}C^2H^5\,*\\C^2H^5O\end{matrix}\right.}$$

$$\underset{\text{Zinc-monethyl-ethylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ZnC^2H^5\\C^2H^5\end{matrix}\right\}O^2} + 2H^2O = \underset{\text{Ethylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\H\\C^2H^5\end{matrix}\right\}O^2} + \underset{\text{Alcohol.}}{\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O^6} + \underset{\text{Zinc-hydrate.}}{\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2}$$

In this and in all the analogous reactions, it is found advantageous to use, instead of zinc-ethyl, &c., a mixture of ethylic iodide and amalgamated zinc, whereby the organo-zinc compound is generated during the reaction, and the trouble of specially preparing it is saved. The whole operation then proceeds at the ordinary atmospheric pressure, and a larger product is obtained. The first stage of the reaction in the production of leucic ether may then be represented as follows:

$$\left.\begin{matrix}(C^2O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2 + 4C^2H^5I + Zn^4 = \left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ZnC^2H^5\\C^2H^5\end{matrix}\right\}O^2 + Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5O\end{matrix}\right. + 2Zn''I^2.$$

Ethylic leucate or diethoxalate has been already described as leucic ether (iii. 578). When treated with *trichloride of phosphorus*, it yields ethylic ethocrotonate, $\left.\begin{matrix}C^4H^4(C^2H^5)O\\C^2H^5\end{matrix}\right\}O$, whence may be obtained ethocrotonic acid, $\left.\begin{matrix}C^4H^4(C^2H^5)O\\H\end{matrix}\right\}O = C^6H^{10}O^2$, isomeric with pyroterebic acid (*vid. sup.*).

Zinc-ethyl acts violently on it, each drop on coming in contact with the ether, even if previously cooled by a freezing mixture, hissing like phosphoric anhydride dropt into water. The product of the reaction is zincmonethyl-ethylic leucate, the change consisting in the substitution of zinc-monethyl for hydrogen, and being accompanied by the evolution of torrents of ethylic hydride:

$$C^6H^{11}(C^2H^5)O^3 + Zn''(C^2H^5)^2 = C^6H^{10}(ZnC^2H^5)'(C^2H^5)O^3 + C^2H^6.$$

Zinc-monethyl-ethylic leucate is a colourless viscous solid, soluble in ether, but apparently incapable of crystallisation. It absorbs oxygen with avidity, and effervesces strongly in contact with water, reproducing leucic ether:

$$C^6H^{10}(ZnC^2H^5)(C^2H^5)O^3 + 2H^2O = C^6H^{11}(C^2H^5)O^3 + C^2H^6 + Zn''H^2O^2.$$

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* See page 225.

Iodine acts strongly upon it, producing zincoleucic ether, iodide of ethyl, and iodide of zinc:

$$\underset{\text{Zinc-monethyl-ethylic leucate.}}{2C^6H^{10}(ZnC^2H^5)(C^2H^5)O^3} + I^4 = \underset{\text{Zincoleucic ether.}}{C^{12}H^{20}Zn''(C^2H^5)^2O^6} + Zn''I^2 + 2C^2H^5I.$$

*Methylic Diethoxalate.* A mixture of 4 at. ethylic iodide and 1 at. methylic oxalate, digested with zinc for about 96 hours at 30°—50°, solidifies to a mass of crystals, which when treated with water and distilled, yields ethylic alcohol, and an ether having the composition of diethoxalate or leucate of methyl:

$$\underset{\text{Methylic oxalate.}}{\left.\begin{matrix}(C^2O^2)''\\ CH^3\\ CH^3\end{matrix}\right\}O^2} + 4C^2H^5I + Zn^4 = \underset{\text{Zinc-monethyl-methylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ ZnC^2H^5\\ CH^3\end{matrix}\right\}O^2} + \underset{\text{Zinc-methyl-ethylate.}}{Zn''\left\{\begin{matrix}CH^3\\ C^2H^5O\end{matrix}\right.} + 2Zn''I^2.$$

$$\underset{\text{Zinc-monethyl-methylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ ZnC^2H^5\\ CH^3\end{matrix}\right\}O^2} + 2H^2O = \underset{\text{Methylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ H\\ CH^3\end{matrix}\right\}O^2} + \underset{\text{Ethylic hydride.}}{\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}} + Zn''H^2O^2.$$

Methylic leucate is a colourless, transparent, tolerably mobile liquid, having a peculiar odour, not much like that of ethylic leucate, sparingly soluble in water, easily in alcohol or ether. Specific gravity = 0·9896 at 16·5°. Boils at 165° and distils unchanged. Vapour-density, obs. = 4·84; calc. = 5·03.

Methylic leucate is easily decomposed by alkaline bases, yielding methylic alcohol and metallic leucates. The *barium-salt*, $C^{12}H^{22}Ba''O^6$, thus obtained is a crystalline mass very soluble in water, alcohol, and ether. On decomposing it with sulphuric acid and evaporating the filtrate, diethoxalic or leucic acid is obtained in splendid crystals which sublime readily at 50°, slowly even at common temperatures, and melt at 74·5°. In these respects the acid thus obtained agrees with ordinary leucic acid, and with that obtained by the action of zinc-ethyl on oxalic ether; but the silver-salts of the two acids differ in certain respects, that obtained from methylic leucate crystallising in anhydrous silky fibres which are scarcely discoloured at 100°, whereas that obtained from ethylic leucate forms brilliant radiate needles containing ½ at. water, which it does not give up at 100°, though it suffers rapid discoloration at that temperature. It is possible therefore that the diethoxalic or leucic acids obtained by the action of zinc-ethyl on the oxalates of ethyl and methyl respectively may not be absolutely identical, but only isomeric.

*Amylic Diethoxalate.* A mixture of amylic oxalate and ethylic iodide in equivalent proportions digested with zinc for several days at 50°—60°, and subsequently treated with water, yields in like manner a distillate containing amylic diethoxalate or leucate, $C^{11}H^{22}O^3$; thus:

$$\underset{\text{Amylic oxalate.}}{\left.\begin{matrix}(C^2O^2)''\\ C^5H^{11}\\ C^5H^{11}\end{matrix}\right\}O^2} + 4C^2H^5I + Zn^4 = \underset{\text{Amylic zinc-monethylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O)''\\ ZnC^2H^5\\ C^5H^{11}\end{matrix}\right\}O^2} + \underset{\text{Zinc-ethylo-amylate.}}{Zn''\left\{\begin{matrix}C^2H^5\\ C^5H^{11}O\end{matrix}\right.} + 2ZnI^2.$$

$$\underset{\text{Amylic zinc-monethylo-leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ ZnC^2H^5\\ C^5H^{11}\end{matrix}\right\}O^2} + 2H^2O = \underset{\text{Amylic leucate.}}{\left.\begin{matrix}[C^2(C^2H^5)^2O]''\\ H\\ C^5H^{11}\end{matrix}\right\}O^2} + \left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\} + Zn''H^2O^2.$$

Amylic leucate is a colourless, transparent, slightly oily liquid, having a fragrant and somewhat amylic odour; insoluble in water, but soluble in all proportions in alcohol and ether. Specific gravity = 0·93227 at 13°. Boils constantly at 225°. Vapour-density obs. = 6·74; calc. = 6·97. The boiling point and specific gravity in the liquid state of this ether are almost identical with those of its isomer, ethylic ethamoxalate (p. 276).

**Dimethoxalic** or **Dimethoglycollic Acid.** $C^4H^8O^3 = \left.\begin{matrix}[C^2(CH^3)^2O]''\\ H^2\end{matrix}\right\}O^2$.—A mixture of 1 at. methylic oxalate and 4 at. methylic iodide treated with amalgamated zinc as above described, solidifies to a yellowish gummy mass, which when distilled with water, yields methylic alcohol, and leaves a residue of iodide, oxalate and dimethoxalate of zinc. The reaction is doubtless exactly similar to that of zinc and ethylic iodide on ethylic oxalate (p. 273), and might be represented by perfectly similar equations, substituting methyl for ethyl; but the resulting dimethoxalate of methyl appears to be very unstable, and to be decomposed by the hydrate of zinc as fast as it is formed, and converted into dimethoxalate of zinc, $C^8H^{14}Zn''O^6$. This zinc-salt treated with baryta-water yields dimethoxalate of barium, $C^8H^{14}Ba''O^6$, which crystallises in brilliant needles, neutral, having the odour of fresh butter, very soluble in water and alcohol, nearly insoluble in ether.

*Dimethoxalic acid*, $C^4H^8O^3$, obtained by decomposing the barium-salt with sulphuric acid and agitating the filtrate with ether, crystallises by evaporation in large prisms, melts at 75·7° and sublimes at 50° in very fine prismatic crystals; boils at 212° and distils unchanged. It is strongly acid and easily unites with bases, forming crystalline salts. The *silver-salt*, $C^4H^7AgO^3$, crystallises in stellate groups of nacreous scales.

3. **Ethomethoxalic** or **Ethomethoglycollic Acid,** $C^5H^{10}O^3 = \left.\begin{matrix}C^2(C^2H^5)(CH^3)O\\ H^2\end{matrix}\right\}O^2$. —The ethylic ether of this acid is obtained by the action of zinc on a mixture of ethylic oxalate with methylic and ethylic iodides in equivalent proportions. The reaction takes place as shown by the equations:

$$\underset{\text{Ethylic oxalate.}}{\left.\begin{matrix}(C^2O^2)''\\ C^2H^5\\ C^2H^5\end{matrix}\right\}O^2} + 2CH^3I + 2C^2H^5I + Zn^4 =$$

$$\underset{\substack{\text{Zinc-monomethyl-etho-}\\ \text{methoxalate of ethyl.}}}{\left.\begin{matrix}[C^2(CH^3)(C^2H^5)O]''\\ ZnCH^3\\ C^2H^5\end{matrix}\right\}O^2} + \underset{\substack{\text{Zinc ethylo-}\\ \text{ethylate.}}}{Zn''\left\{\begin{matrix}C^2H^5\\ C^2H^5O\end{matrix}\right.} + 2ZnI^2.$$

$$\underset{\substack{\text{Zinc-monomethyl-etho-}\\ \text{methoxalate of ethyl.}}}{\left.\begin{matrix}[C^2(CH^3)(C^2H^5)O]''\\ ZnCH^3\\ C^2H^5\end{matrix}\right\}O^2} + 2H^2O = \underset{\substack{\text{Ethylic etho-}\\ \text{methoxalate.}}}{\left.\begin{matrix}[C^2(CH^3)(C^2H^5)O]''\\ H\\ C^2H^5\end{matrix}\right\}O^2} + \left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\} + Zn''H^2C^2.$$

Ethylic ethomethoxalate, $C^7H^{14}O^3$, is a colourless, transparent, mobile liquid possessing a penetrating ethereal odour much like that of leucic ether. It is very soluble in water, alcohol, and ether. Specific gravity = 0·9768 at 13°. Boils at 165·5°. Vapour-density, obs. = 4·98; calc. = 5·04. It is easily decomposed by aqueous solutions of the *alkalis* and of *baryta*. *Trichloride of phosphorus* converts it into the ethylic ether of methocrotonic acid, $C^5H^8O^2$, isomeric with angelic acid (p. 273).

*Ethomethoxalate of Barium*, $C^{10}H^{18}Ba''O^6$, is very soluble in water, and crystallises from aqueous solution as a beautifully radiated mass having a silky lustre.

*Ethomethoxalate of Hydrogen*, or *Ethomethoxalic acid*, $C^5H^{10}O^3$, is obtained by evaporation, first in a retort, afterwards in vacuo, as a splendid white crystalline mass, melting at 63°, subliming readily at 100°, and condensing on a solid surface in magnificent star-like groups. It boils with decomposition at 190°. It dissolves very easily in water, alcohol, and ether; small fragments of it thrown on water rotate like camphor whilst dissolving. The solutions are strongly acid and easily decompose carbonates.

*Ethomethoxalate of Silver*, $C^5H^9AgO^3$, crystallises in splendid mammellated masses, moderately soluble in water.

4. **Amhydroxalic** or **Amoglycollic Acid.** $C^7H^{14}O^3 = \left.\begin{matrix}[C^2H(C^5H^{11})O]''\\ H^2\end{matrix}\right\}O^2$. —The ethylic ether of this acid is produced, together with two others, by the action of zinc on a mixture of ethylic oxalate and amylic iodide. When a mixture of these ethers in equivalent proportion is digested with granulated zinc at 70°, the zinc is gradually dissolved, while much amylic hydride and amylene are given off. The mixture finally assumes a viscous or semisolid condition, and when treated with water yields a further quantity of amylic hydride which distils off at a gentle heat. On increasing the temperature, water passes over accompanied by amylic alcohol, amylic iodide, and an ethereal liquid which, after drying with chloride of calcium, begins to boil at 132°, the product which first passes over consisting principally of amylic alcohol mixed with amylic iodide. Afterwards the thermometer rises rapidly to 200°, between which temperature and 205°, ethylic amhydroxalate, $C^9H^{18}O^3$, passes over. A second rapid rise of temperature then occurs till the thermometer remains stationary between 222° and 226°, at which temperature ethylic ethamoxalate, $C^{11}H^{22}O^3$, passes over. Lastly, the temperature rises to 260°—264°, between which points ethylic diamoxalate, $C^{14}H^{28}O^3$, distils over. These several ethers are further purified by repeated fractional distillation.

The formation of ethylic amhydroxylate is represented by the equations,

$$\left.\begin{array}{c}(C^2O^2)''\\ C^2H^5\\ C^2H^5\end{array}\right\}O^2 + 4C^5H^{11}I + Zn^4 = \left.\begin{array}{c}[C^2(C^5H^{11})(ZnC^5H^{11})O]''\\ ZnC^5H^{11}\\ C^2H^5\end{array}\right\}O^2 + Zn\left\{\begin{array}{l}C^5H^{11}\\ C^2H^5O\end{array}\right. + 2ZnI^2.$$

$$\left.\begin{array}{c}[C^2(C^5H^{11})(ZnC^5H^{11})O]''\\ ZnC^5H^{11}\\ C^2H^5\end{array}\right\}O^2 + 4H^2O =$$

$$\left.\begin{array}{c}[C^2H(C^5H^{11})O]''\\ H\\ C^2H^5\end{array}\right\}O^2 + \left.\begin{array}{c}C^5H^{11}\\ H\end{array}\right\}O + \left.\begin{array}{c}C^5H^{11}\\ H\end{array}\right\} + 2Zn''H^2O^2.$$

The compound $C^{19}H^{38}Zn''O^3$ formed in the first stage of the reaction consists of oxalic ether in which an atom of oxygen is replaced half by amyl and half by zinc-monamyl, whilst a second atom of zinc-monamyl is substituted for one of ethyl.

*Ethylic amhydroxalate*, $C^9H^{18}O^3 = \left.\begin{array}{c}C^2H(C^5H^{11})O\\ H\\ C^2H^5\end{array}\right\}O^2$, is a somewhat oily, transparent, slightly straw-coloured liquid, of specific gravity 0·9449 at 13°, having a pleasant aromatic odour and burning taste. It boils at 203°. Vapour-density, obs., = 5·47; calc. = 6·0.

*Amhydroxalate of Barium*, $C^{14}H^{26}Ba''O^6$, crystallises in large beautiful nacreous scales like paraffin, moderately soluble. The *calcium-salt*, $C^{14}H^{26}Ca''O^6$, forms a white crystalline mass.

The *hydrogen-salt* or *amhydroxalic acid*, $C^7H^{14}O^3$, prepared from the zinc-salt which is contained in the residue remaining after the distillation of the three ethers above described, is but sparingly soluble in water, from which, however, it crystallises in beautiful nacreous scales which melt at 60·5°, but afterwards remain liquid for some time even at ordinary temperatures; they are very unctuous to the touch, and easily soluble in alcohol and ether.

The *copper-salt*, $C^{14}H^{26}Cu''O^6$, is deposited from its aqueous solution in minute light blue scales, very sparingly soluble in water.

5. **Ethamoxalic** or **Ethamoglycollic Acid,** $C^9H^{18}O^3 = \left.\begin{array}{c}[C^2(C^2H^5)(C^5H^{11})O]''\\ H^2\end{array}\right\}O^2$. —The ethylic ether of this acid, $C^{11}H^{22}O^3$, is the portion of the ethereal distillate above mentioned, which boils between 222° and 226°. Its formation is represented by the equations:

$$\left.\begin{array}{c}C^2O^2\\ C^2H^5\\ C^2H^5\end{array}\right\}O^2 + 4C^5H^{11}I + Zn^4 = \left.\begin{array}{c}[C^2(C^5H^{11})(ZnC^5H^{11})O]''\\ C^2H^5\\ C^2H^5\end{array}\right\}O^2 + Zn''\left\{\begin{array}{l}C^5H^{11}\\ C^5H^{11}O\end{array}\right. + 2ZnI^2.$$

$$\left.\begin{array}{c}[C^2(C^5H^{11})(ZnC^5H^{11})O]''\\ (C^2H^5)^2\end{array}\right\}O^2 + 2H^2O =$$

$$\underset{\text{Ethylic ethamoxalate.}}{\left.\begin{array}{c}[C^2(C^2H^5)(C^5H^{11})O]''\\ H\\ C^2H^5\end{array}\right\}}O^2 + \left.\begin{array}{c}C^5H^{11}\\ H\end{array}\right\} + Zn''H^2O^2.$$

Ethylic ethamoxalate is a straw-coloured oily liquid, having an aromatic but somewhat amylic odour and a burning taste. Specific gravity = 0·9399 at 13°. Boiling point between 224° and 225°. Vapour-density, obs. = 6·29; calc. = 6·92.

By decomposing this ether with alcoholic potash, adding sulphuric acid in excess, and treating the product with ether, ethamoxalic acid is obtained as a thick oil, gradually solidifying to a crystalline mass. The *barium-salt* contains $C^{18}H^{34}Ba''O^6$; the *silver-salt*, $C^9H^{17}AgO^3$.

6. **Diamoxalic** or **Diamoglycollic Acid,** $C^{12}H^{24}O^3 = \left.\begin{array}{c}[C^2(C^5H^{11})^2O]''\\ H^2\end{array}\right\}O$.—The ethylic ether of this acid, $C^{14}H^{28}O^3$, is contained in the last portion of the ethereal distillate resulting from the action of zinc and iodide of amyl on oxalic ether. Its formation is represented by the equations:

$$\underset{\text{Ethylic oxalate.}}{\left.\begin{array}{c}(C^2O^2)''\\ C^2H^5\\ C^2H^5\end{array}\right\}}O^2 + 4C^5H^{11}I + Zn^4 = \underset{\text{Ethylic zinc-monamyl-diamoxalate.}}{\left.\begin{array}{c}[C^2(C^5H^{11})^2O]''\\ ZnC^5H^{11}\\ C^2H^5\end{array}\right\}}O^2 + \underset{\text{Zinc-amylo-ethylate.}}{Zn''\left\{\begin{array}{l}C^5H^{11}\\ C^2H^5O\end{array}\right.} + 2ZnI^2.$$

$$\underset{\text{Ethylic zinc monamyl-diamoxalate.}}{\left.\begin{array}{c}[C^2(C^5H^{11})^2O]''\\ ZnC^5H^{11}\\ C^2H^5\end{array}\right\}}O^2 + 2H^2O = \underset{\text{Ethylic diamoxalate.}}{\left.\begin{array}{c}[C^2(C^5H^{11})^2O]''\\ H\\ C^2H^5\end{array}\right\}}O^2 + \left.\begin{array}{c}C^5H^{11}\\ H\end{array}\right\} + Zn''H^2O^2.$$

*Ethylic diamoxalate* is more viscid than the two last-described ethers, and has the lowest specific gravity of any ether belonging to this series, its density at 13° being only 0·9137. In fact the specific gravities of all these ethers decrease as their atomic weights increase. Their vapours also exhibit a tendency to dissociation, increasing with the weight of the atoms which replace the oxygen in oxalic ether, whence there arises an increasing divergence between the observed and calculated vapour-densities. The vapour-density of ethylic diamoxalate is by experiment 8·4, by calculation only 5·9. Boiling point about 262°.

*Diamoxalate of Barium*, $C^{24}H^{46}Ba''O^6$, obtained by decomposing the ether with baryta-water, crystallises in minute elastic needles having the appearance of wool when dry. It is moderately soluble in hot, sparingly in cold water.

*Diamoxalic acid*, obtained by decomposing a solution of the barium-salt in hot dilute alcohol with sulphuric acid, and evaporating the filtrate, crystallises in colourless satiny fibres, insoluble in water, but soluble in alcohol and ether. It melts at 122°, and solidifies immediately after a very slight reduction of temperature. At a stronger heat it sublimes and condenses on a cold surface in white crystalline flakes like snow.

7. *Action of Zinc on a mixture of Amylic oxalate and Amylic iodide.* When these ethers in equivalent quantities are gently heated with zinc, a brisk reaction soon sets in, much amylic hydride and amylene are evolved, and the whole solidifies to a gum-like mass, which when distilled with water yields an oily liquid resembling that obtained when ethylic oxalate is used, and in all probability containing a series of amylic ethers analogous to the ethylic ethers described under 4, 5 and 6; but it has not yet been found possible to separate them, their boiling points being so high that they decompose when an attempt is made to distil them.

**OXALITE.** Native ferrous oxalate, also called *Humboldtine* (p. 258).

**OXALMETHYLOVINIDE.** Syn. with METHYLETHYLIC OXALATE (p. 271).

**OXALOVINIC ACID.** Syn. with ETHYLOXALIC ACID (p. 271).

**OXALURAMIDE.** *Oxalan.* $C^3H^5N^3O^3 = \left.\begin{matrix}C^3H^3N^2O^3\\H^2\end{matrix}\right\}N$ or $\left.\begin{matrix}(C^2O^2)''\\(CO)''\\H^5\end{matrix}\right\}N^3$.

(Rosing and Schischkoff, Ann. Ch. Pharm. cvi. 255.—Liebig, *ibid.* cviii. 126.—Strecker, *ibid.* cxiii. 47).—A compound obtained as a white precipitate, together with dialuric acid, by the action of ammonia and hydrocyanic acid on alloxan:

$$\underset{\text{Alloxan.}}{2C^4H^2N^2O^4} + H^2O + NH^3 = \underset{\text{Oxaluramide.}}{C^3H^5N^3O^3} + \underset{\text{Dialuric acid.}}{C^4H^4N^2O^4} + CO^2.$$

Probably also by the action of anhydrous ammonia on parabanic acid:

$$C^3H^2N^2O^3 + NH^3 = C^3H^5N^3O^3 \text{ (Strecker).}$$

It was first prepared by Rosing and Schischkoff, who called it *oxalan*, and assigned to it the formula $C^{15}H^{24}N^{14}O^{15}$. Its formation, however, appears to have been previously observed by Liebig, and analyses of it subsequently made under his direction do not agree with Rosing and Schischkoff's formula, but show, in accordance also with Strecker's analysis, that the body has the composition of oxaluramide:

| | *Calculation.* | | Rosing and Schischkoff. | | Liebig. | | Strecker. |
|---|---|---|---|---|---|---|---|
| $C^3$ | 36 | 27·5 | 27·0 | 27·7 | 26·3 | 27·7 | 27·7 |
| $H^5$ | 5 | 3·8 | 4·0 | 4·4 | 4·0 | 4·2 | 3·8 |
| $N^3$ | 42 | 32·1 | 30·3 | 30·1 | 32·6 | 32·4 | 32·4 |
| $O^3$ | 48 | 36·6 | | | | | |
| | 131 | 100·0 | | | | | |

Strecker has also shown that the hydrocyanic acid takes no part in the reaction, further than as a sort of ferment, and that the whole of it may be recovered from the liquid filtered from the precipitate of oxaluramide.

Oxaluramide is a white crystalline powder, insoluble in cold *water*, but dissolved and decomposed by prolonged boiling with water, with formation of oxalurate and oxalate of ammonium. When boiled with caustic *alkalis*, it gives off ammonia and yields an oxalate. It dissolves completely in strong *sulphuric acid*, and according to Strecker is precipitated from the solution by water, in its original state. According to Rosing and Schischkoff, on the other hand, the body thus precipitated is a product of decomposition, containing $C^{11}H^{16}N^{12}O^{13}$; moreover the dilute solution from which this compound has separated deposits after a while large colourless prisms containing $C^8H^{18}N^4O^9$. According to Strecker, however, this last body is nothing but alloxantin ($C^8H^{10}N^4O^{10}$), formed by the action of the acid on dialurate of ammonium adhering to the oxaluramide.

A solution of alloxan mixed with hydrocyanic acid yields, on addition of ethylamine, phenylamine, &c., precipitates resembling oxaluramide and consisting of ethyl-oxaluramide, $C^3H^4(C^2H^5)N^3O^3$, phenyl-oxaluramide, $C^3H^4(C^6H^5)N^3O^3$, &c. (Strecker.)

The last-mentioned body is identical with that which Laurent and Gerhardt obtained by heating parabanic acid with aniline. It is a white slightly nacreous crystalline powder, composed of well-defined microscopic needles, tasteless and inodorous, insoluble in boiling water, nearly insoluble in boiling alcohol; it melts at a high temperature, and decomposes when still more strongly heated, giving off very acrid vapours containing cyanogen-compounds. When slightly heated with potash, it gives off aniline and ammonia. It dissolves easily in sulphuric acid, the solution when heated giving off carbonic anhydride and carbonic oxide, without blackening; and the product, if exposed to the air, gradually becomes filled with crystals of acid sulphate of ammonium, and yields, when diluted with water, the reaction of phenyl-sulphuric acid. (Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 177.)

**OXALURANILIDE.** Syn. with PHENYL-OXALURAMIDE (*vid. sup.*).

**OXALURIC ACID.** $C^3H^4N^2O^4$. (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 287.)—When parabanic acid is heated with aqueous ammonia, it is converted into oxalurate of ammonium; or carbonate of calcium dissolved in aqueous parabanic acid yields oxalurate of calcium. Oxalurate of ammonium is also formed by the action of oxygen on an aqueous solution of murexan (see MUREXAN); and by adding ammonia to a solution of uric acid in warm, very dilute, nitric acid. The ammonium-salt is dissolved in warm water, and the oxaluric acid precipitated by a mineral acid, washed and dried (Liebig and Wöhler). Lastly, oxaluric acid is produced, together with guanidine, parabanic acid, xanthine, and urea, by the action of hydrochloric acid and potassic chlorate on guanine. (Strecker, Ann. Ch. Pharm. cxviii. 151.)

Oxaluric acid is a white crystalline powder, which has a very acid taste, and reddens litmus. It neutralises alkalis completely. It is very sparingly soluble in cold water: its aqueous solution is decomposed by boiling into oxalic acid and urea:

$$C^3H^4N^2O^4 + H^2O = C^2H^2O^4 + CH^4N^2O.$$

Oxaluric acid is monobasic. The *ammonium-salt*, $C^3H^3(NH^4)N^2O^4$, forms silky anhydrous needles, readily soluble in hot water (Liebig and Wöhler). The *barium-salt*, $C^6H^6Ba''N^4O^8.2H^2O$, is obtained by precipitation in long colourless needles, often intersecting one another. It gives off its water at 130°; the crystals dissolve in 633 pts. water at 9° and 55 pts. at 100°.—The *calcium-salt*, $C^6H^6Ca''N^4O^8.2H^2O$, obtained in like manner, crystallises in colourless needles, soluble in 483 pts. water at 15°, and in 20 pts. boiling water (P. Waage, Ann. Ch. Pharm. cxviii. 501).—The *silver-salt* is obtained by adding oxalurate of ammonium to nitrate of silver, as a flaky precipitate which dissolves in hot water and separates on cooling in long silky anhydrous needles (Liebig and Wöhler). The *sodium-salt* separates as a crystalline powder on mixing a dilute lukewarm solution of sodic carbonate with a solution of alloxan containing a little prussic acid. It is much less soluble in water than the potassium-salt. (Waage.)

Oxaluric acid may be regarded as an *uridic acid* analogous to the amic acids: $C^3H^4N^2O^4$ = oxalic acid + urea − $H^2O$, just as oxamic acid, $C^2H^3NO^3$ = oxalic acid + ammonia − $H^2O$. (Gerhardt and Laurent, Ann. Ch. Phys. [3] xxiv. 175.)

F. T. C.

**OXALVINOMETHYLIDE.** Syn. with METHYL-ETHYLIC OXALATE (p. 271).

**OXAMETHANE.** Syn. with ETHYLIC OXAMATE (p. 280).

**OXAMETHYLANE.** Syn. with METHYLIC OXAMATE (p. 281).

**OXAMIC ACID.** $C^2H^3NO^3$ =

$\left.\begin{matrix}H^3\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Balard, Ann. Ch. Phys. [3] iv. 93.—Bacaloglio, J. pr. Chem. lxxxi. 369.—Toussaint, Ann. Ch. Pharm. cxx. 237.)—An acid produced by the dehydration of acid oxalate of ammonium. This salt when heated in an oil-bath to about 230°, gives off water, carbonic oxide, and carbonic anhydride, then carbonate and cyanide of ammonium, and if the distillation has not been carried too far, a residue is left consisting almost entirely of oxamide and oxamic acid. The formation of the latter is represented by the equation:

$$C^2H(NH^4)O^4 - H^2O = C^2H^3NO^3.$$

The acid residue is treated with cold water; the filtered solution is neutralised with ammonia and precipitated by a saturated solution of a barium-salt; and the resulting crystalline precipitate of oxamate of barium purified by solution in boiling water (decolorising with animal charcoal if necessary) and crystallisation. The crystals are then decomposed with an equivalent quantity of very dilute sulphuric acid, and the filtrate is evaporated to the crystallising point.

The acid may also be obtained by decomposing the silver-salt with dry hydrochloric acid gas, treating the product with boiling absolute alcohol, and evaporating the filtrate.

Oxamic acid is also produced, as an ammonium-salt, by boiling oxamide with aqueous ammonia:

$$C^2H^4N^2O^2 + H^2O = C^2H^2(NH^4)NO^3.$$

After the boiling has been continued for some time, the ammonia being always kept in excess, the solution on cooling deposits nothing but groups of slender prisms, consisting of ammonium-oxamate; and the saturated solution of this salt mixed with strong hydrochloric acid, and left to itself for twelve hours, deposits oxamic acid as a white powder, which may be washed with cold water and left to dry at the ordinary temperature. (Toussaint.)

Oxamic acid is a white crystalline powder sparingly soluble in cold water, still less soluble in alcohol, insoluble in ether. According to Toussaint, it dissolves in 58 pts. water at 18°; in another experiment with the acid separated from mercurous oxamate he found that it required 71 pts. water at 14° to dissolve it. By boiling with water it is quickly converted into acid oxalate of ammonium. Heated with caustic alkalis or with acids it is resolved into ammonia and oxalic acid. It melts at 173°, and is decomposed into water, oxamide and formic acid. (Toussaint.)

Oxamates. Oxamic acid is monobasic, the formula of its salts being $C^2H^2MNO^3$ or $C^4H^4M''N^2O^6$, according to the atomicity of the metal. The *ammonium-salt* $C^2H^2(NH^4)NO^3$ forms stellate groups of small anhydrous prisms, which according to Sénarmont (Jahresb. 1857, p. 296) are monoclinic, exhibiting the combination $\infty P . [\infty P2] . [\infty P\infty] . oP$. The clinodiagonal is to the orthodiagonal as 0·6489 : 1. Angle of inclined axes = 64° 23′; $\infty P : \infty P$ in the clinodiagonal principal section = 119° 20′; $[\infty P2] : [\infty P2]$, in the same = 81° 2′; $oP : \infty P$ = 111° 55′.—The *barium-salt*, $C^4H^4Ba''N^2O^6.3H^2O$, is a crystalline precipitate which gives off its water at 150° (Balard).—The *cupric salt*, $C^4H^4Cu''N^2O^6.H^2O$, is obtained by precipitation as a blue granular powder soluble in hydrochloric acid, less soluble in water and in nitric acid. The hydrochloric acid solution of the precipitate is coloured blue by potash, but precipitated only at the boiling heat (Bacaloglio).—The *ferrous salt*, $C^4H^4Fe''N^2O^6.H^2O$, forms yellow microscopic crystals. Recently precipitated *ferric hydrate* dissolves in boiling aqueous oxamic acid; but the solution decomposes, like the oxalate, on exposure to the sunshine, forming a yellow precipitate. The solution of ferric hydrate in acid oxamate of potassium deposits green crystals on cooling (Bacaloglio).—The *neutral lead-salt*, $C^4H^4Pb''N^2O^6.H^2O$, is white, crystalline, sparingly soluble in cold, more easily in hot water; the solution has an acid reaction. The salt gives off its water (4·49 per cent.) at 100°, but does not decompose at 175°. The *basic lead-salt*, $C^4H^4Pb''N^2O^6.Pb''O$, obtained by precipitating basic acetate of lead with ammonium-oxamate, is a white precipitate, insoluble in water and anhydrous after being treated with boiling water (Bacaloglio).—The *mercurous* and *mercuric salts* are white precipitates, obtained by heating the solutions of the nitrates with ammonium oxamate (Bacaloglio).—The *nickel-salt*, $C^4H^4Ni''N^2O^6.H^2O$, is a greenish-white granular powder sparingly soluble in hot water (Bacaloglio).—The *silver-salt*, $C^2H^2AgNO^3$, obtained by treating a solution of silver-nitrate with barium-oxamate, separates as the liquid cools in colourless silky needles, which are decomposed by exposure to the light, the silver separating on the surface and blackening them. (Balard.)

**OXAMIC ETHERS.** In the molecule of oxamic acid $\left.\begin{matrix}H^2\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, either the hydrogen belonging to the water-type, or that belonging to the ammonia-type, may be replaced by alcohol-radicles. In the former case neutral ethers are formed, belonging to the class of amethanes (i. 198), of which the following are known:

Methylic Oxamate or Oxamethylane . . $C^3H^5NO^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\CH^3\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

Ethylic Oxamate or Oxamethane . . $C^4H^7NO^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

Amylic Oxamate or Oxamylane . . $C^7H^{13}NO^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\C^5H^{11}\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

They are produced by the action of dry ammonia on the corresponding neutral oxalic ethers.

In the latter case, monobasic acid ethers are produced, which, if only one atom of hydrogen is replaced, are metameric with those of the preceding class containing the same alcohol-radicles. They are obtained by dehydration of the acid oxalates of the corresponding amines. The following have been prepared:

Methyl-oxamic acid . . . $C^3H^5NO^3 = \left.\begin{matrix}H.CH^3\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

Ethyl-oxamic acid . . . $C^4H^7NO^3 = \left.\begin{matrix}H.C^2H^5\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

Phenyl-oxamic acid . . . $C^8H^7NO^3 = \left.\begin{matrix}H.C^6H^5\\(C^2O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

The replacement of both hydrogen-atoms belonging to the ammonia-type would likewise yield monobasic acids: none of these are however known in the free state, but the ethylic ethers of dimethyl- and diethyl-oxamic acids have been obtained, viz.:

Ethylic Dimethyloxamate . . $C^6H^{11}NO^3 = \left.\begin{matrix}(CH^3)^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

Ethylic Diethyloxamate . . $C^8H^{15}NO^3 = \left.\begin{matrix}(C^2H^5)^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$

**Amylic Oxamate,** or **Oxamylane.** $C^7H^{13}NO^3$.—This compound is produced by the action of ammonia in the gaseous state or in alcoholic solution on neutral amylic oxalate:

$$\left.\begin{matrix}(C^2O^2)''\\(C^5H^{11})^2\end{matrix}\right\}O^2 + NH^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\C^5H^{11}\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} + \left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O.$$

It is soluble in alcohol, whence it separates on evaporation in rudimentary ill-defined crystals. It is decomposed by boiling water, yielding amylic alcohol and oxamic acid.

**Ethylic Oxamates.**—*a. Oxamethane.* $C^4H^7NO^3 = \left.\begin{matrix}H^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—(Dumas and Boullay, Ann. Ch. Phys. [2] xxxvii. 40.—Dumas, *ibid.* liv. 241.—Liebig, Ann. Ch. Pharm. ix. 129).—Prepared by passing dry ammonia gas through dry ethylic oxalate till it solidifies. The resulting mass is washed with alcohol, and the solution is evaporated till it crystallises.

Oxamethane forms unctuous pearly crystals belonging to the trimetric system. Dominant form, $\breve{P}\infty$ . $\infty\bar{P}\infty$ . $\infty P$ . $\infty\breve{P}2$. Ratio of axes, $a : b : c = 0{\cdot}924 : 1 : 0{\cdot}715$. Angle $\breve{P}\infty : \infty\bar{P}\infty = 125° 33'$; $\infty P : \infty\bar{P}\infty = 132° 43'$; $\infty\breve{P}2 : \infty\bar{P}\infty = 151° 34'$. It melts at 110° and distils at 220°. Vapour-density (calc. for 2 vol.) = 4·056 It dissolves very readily in cold *water* and in *alcohol.* By boiling with *water* it is converted into alcohol and acid oxalate of ammonium:

$$C^4H^7NO^3 + 2H^2O = C^2H(NH^4)O^4 + C^2H^6O.$$

*Ammonia* converts it into alcohol and oxamide:

$$C^4H^7NO^3 + NH^3 = C^2H^6O + C^2H^4N^2O^2.$$

According to Balard, the aqueous solution of oxamethane boiled with a small quantity of ammonia, yields oxamate of ammonium. Boiled with *baryta-water* it gives off ammonia and forms a sparingly soluble barium-salt. *Potash* and *soda* under the same circumstances eliminate ammonia and form ethyl-oxalates.

*β. Chloroxamethane,* $C^4H^2Cl^5NO^3$. *Chloroxethamide.* (Malaguti, Ann. Ch. Phys. lxxiv. 304; *ibid.* [3] xv. 49).—Produced by the action of dry ammonia-gas on perchloroxalic ether:

$$\underset{\text{Perchloroxalic ether.}}{C^2(C^2Cl^5)^2O^4} + 2NH^3 = \underset{\text{Chloroxamethane.}}{C^4H^2Cl^5NO^3} + \underset{\text{Trichloracetamide.}}{C^2H^2Cl^3NO} + 2HCl.$$

When dry ammonia-gas is passed into a tubulated retort containing pulverised perchloroxalic ether, the temperature rises, a flocculent substance is deposited on the sides of the retort, and a fetid odour is evolved. When the action has ceased, the retort is found to be lined with small iridescent laminæ. The whole is treated with ether, the solution filtered from sal-ammoniac, and the crystals which form on evaporation are pressed between paper and purified by solution in hot water, treatment with animal charcoal, and repeated crystallisation.

Chloroxamethane forms white crystals belonging to the trimetric system, and isomorphous with oxamethane. Dominant form, $\bar{P}\infty$ . $\infty\breve{P}\frac{3}{2}$ . $\infty\bar{P}\infty$. Ratio of the axes $a : b : c = 0{\cdot}924 : 1 : 0{\cdot}715$. Inclination of the faces, $\bar{P}\infty$ . $\bar{P}\infty$ = 125° 33′ : $\infty\breve{P}\frac{3}{2}$ : $\infty\bar{P}\infty$ = 120°; $\infty\breve{P}\frac{3}{2}$ : $\infty\breve{P}\frac{3}{2}$ = 120°. It is sparingly soluble in cold water, very soluble in boiling water, alcohol, and ether; the solution is not precipitated by nitrate of silver or by soluble calcium-salts. It has a saccharine taste, with bitter after-taste. It melts at 134°, but a considerable portion sublimes before melting. Boiling point above 200°.

Boiled for some time with potash, it ultimately disappears, gives off a large quantity of ammonia, and yields oxalate and chloride of potassium, together with another chlorinated salt. Aqueous ammonia dissolves it completely in a few days, producing *chlorethyloxalate of ammonium.*

In consequence of the different behaviour of oxamethane and chloroxamethane with ammonia and potash, Gerhardt and Malaguti suppose that they belong to different types.

γ. *Ethyloxamic acid*, $C^4H^7NO^3 = \left.\begin{matrix} H.C^2H^5 \\ (C^2O^2)'' \\ H \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$.—Formed in small quantity, when oxalate of ethylamine mixed with excess of oxalic acid, is melted for some time in an oil-bath at 180°: $C^2H(C^2H^3N)O^4 - H^2O = C^4H^7NO^3$. (Wurtz, Ann. Ch. Phys. [3] xxx. 465.)

δ. *Ethylic Diethyloxamate*, $C^8H^{15}NO^3 = \left.\begin{matrix} (C^2H^5)^2 \\ (C^2O^2)'' \\ C^2H^5 \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$.—This compound is produced by the action of diethylamine on oxalic ether (ii. 555). It is a liquid which boils at 260°, is resolved by boiling with alkalis into oxalic acid, alcohol, and diethylamine, and, when heated with alcoholic ammonia, is converted into a substance which is isomeric with diethyloxamide, $C^6H^{12}N^2O^2$ (p. 284). (Hofmann, Compt. rend. lii. 902.)

**Methylic Oxamates.** α. *Oxamethylane*, $C^3H^5NO^3$.—Prepared by saturating fused methylic oxalate with dry ammonia gas till the whole solidifies to a crystalline mass. The product dissolved in boiling alcohol crystallises on cooling or evaporation in cubic crystals having a nacreous lustre. When boiled with water to which a few drops of ammonia are added from time to time to neutralise the acid which is produced, the oxamethylane is completely converted into oxamate of ammonium and methylic alcohol. (Dumas and Péligot, Ann. Ch. Phys. [3] lviii. 60.)

β. *Methyloxamic acid*, $C^3H^5NO^3 = \left.\begin{matrix} H.CH^3 \\ (C^2O^2)'' \\ H \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$.—Produced, with elimination of water, by heating acid oxalate of methylamine to about 160°: $C^2H(CH^6N)O^4 - H^2O = C^3H^5NO^3$. Part of the methyloxamic acid remains in the residue, while another portion volatilises, and sometimes forms a crystalline strongly acid sublimate on the neck of the retort. A considerable portion of the acid oxalate of methylamine is, however, converted into neutral oxalate, and subsequently into dimethyloxamide, which also crystallises in the neck of the retort. It is advisable, therefore, to interrupt the distillation after a while, and add a little oxalic acid to the residue. When the decomposition is supposed to be complete, both the distillate and the residue are to be dissolved in hot water, the solution saturated with chalk, and filtered. The concentrated solution deposits, on cooling, a mixture of calcic methyloxamate and dimethyloxamide, which are easily separated by heat, the dimethyloxamide then volatilising, while the calcic methyloxamate remains unaltered; it may be purified by crystallisation from hot water.

Methyloxamic acid forms a crystalline sublimate. The *calcium-salt*, $C^6H^8Ca''N^2O^6$, separates from its hot aqueous solution in small well-defined crystals. (Wurtz, Ann. Ch. Phys. [3] xxx. 465.)

γ. *Ethylic Dimethyloxamate*, $C^6H^{11}NO^3 = \left.\begin{matrix} (CH^3)^2 \\ (C^2O^2)'' \\ C^2H^5 \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$.—Produced, like the corresponding diethyloxamate, by the action of dimethylamine on oxalic ether. It is a liquid boiling between 250° and 260°, and resolved by distillation with potash into alcohol, dimethylamine, and oxalate of potassium. (Hofmann, iii. 998.)

**Phenyloxamic** or **Oxanilic Acid**, $C^8H^7NO^3 = \left.\begin{matrix} H.C^6H^5 \\ (C^2O^2)'' \\ H \end{matrix}\right\}O$ (Laurent and

Liebig (Ann. Ch. Pharm. cxiii. 146) has shown that an aqueous solution of cyanogen Gerhardt, Ann. Ch. Phys. [3] xxiv. 166).—To prepare this compound, aniline mixed with a very large excess of oxalic acid is fused for ten minutes at a high temperature; the cooled mass boiled with water; and the solution filtered from the oxanilide; whereupon it yields, on cooling, crystals of acid oxanilate of aniline, whilst a portion of the salt, together with a small quantity of formanilide and a large quantity of oxalic acid, remains in the mother-liquor, from which, by precipitation at a boiling heat with chloride of calcium, filtering while hot from the oxalate of calcium, and cooling, an additional crop of crystals of calcic oxanilate may be obtained. The above-mentioned brown crystals, which cannot be decolorised by recrystallisation, are converted, either by boiling with baryta-water, or by solution in ammonia and precipitation with chloride of barium, into oxanilate of barium, which must be washed with cold water, and decomposed by boiling with an equivalent quantity of sulphuric acid (an excess decomposes the oxanilic acid), after which the filtrate deposits the oxanilic acid in crystals by evaporation—or they may be converted into the calcium-salt by solution in ammonia and precipitation with chloride of calcium, and that salt decomposed by sulphuric acid mixed with alcohol.

Phenyloxamic acid forms beautiful laminæ, which redden litmus strongly, dissolve sparingly in cold, abundantly in hot *water*, easily in *alcohol*. When heated, it gives off carbonic oxide, carbonic anhydride and water, and is converted into pure oxanilide:

$$2C^8H^7NO^3 \quad = \quad C^{14}H^{12}N^2O^2 \quad + \quad CO \quad + \quad CO^2 \quad + \quad H^2O.$$

By boiling with dilute *hydrochloric* or *sulphuric* acid, it is resolved into hydrochlorate or sulphate of aniline, and free oxalic acid. With a boiling concentrated solution of *potash* it gives off aniline.

The phenyloxamates or oxanilates, which are isomeric with the isatates, give off the whole of their aniline when heated with hydrate of potassium, and a portion when boiled with potash-ley or strong acetic acid.

*Ammonium-salts.*—The *neutral salt*, $C^8H^6(NH^4)NO^3$, forms beautiful laminæ, which dissolve sparingly in cold, very easily in boiling water, and in alcohol.—The *acid salt*, $C^8H^6(NH^4)NO^3.C^8H^7NO^3$, obtained by precipitating the solution of the neutral salt with hydrochloric acid, and leaving the precipitate to crystallise, forms scales, sparingly soluble in cold water. Both salts begin to decompose at 190°, give off ammonia, and afterwards carbonic oxide and carbonic anhydride, together with a small quantity of aniline, and leave oxanilide.

*Barium-salt.*—The white crystalline precipitate, which the ammonium-salt forms with chloride of barium, crystallises from the solution in boiling water, in specular rhombic scales, which contain 29·15 per cent. barium, and are therefore $C^{16}H^{12}Ba''N^2O^6$.

*Calcium-salt.*—Obtained in a similar manner with chloride of calcium. Tufts of needles containing 10·8 per cent. calcium, therefore $C^{16}H^{12}Ca''N^2O^6$.

*Silver-salt.*—Obtained in like manner with nitrate of silver. White tabular crystals which are nearly insoluble in cold, but dissolve readily in hot water. They contain 39·8 per cent. silver: therefore $C^8H^6AgNO^3$.

NITRAZOPHENYLOXAMIC ACID. See NITRAZOPHENYLAMINE, under PHENYLAMINES.

**OXAMIDE.** $C^2H^4N^2O^2 = \left.\begin{matrix}(C^2O^2)''\\ H^4\end{matrix}\right\}N^2$ (Gm. ix. 262; Gerh. i. 275).—This compound was first obtained by Bauhof in 1817, on mixing oxalic ether with aqueous ammonia, but it was regarded as a compound of oxalic ether and ammonia, till Liebig, in 1834, showed it to be identical with the oxamide which Dumas had obtained in 1830 by the action of heat on neutral oxalate of ammonium (p. 252).

When neutral oxalate of ammonium is subjected to dry distillation, till the residue disappears, oxamide is obtained, partly sublimed in the neck of the retort together with carbonate of ammonium, partly floating in flakes on the watery distillate. The whole is suspended in water, and the oxamide, amounting to 4 or 5 per cent. of the ammonium salt, is collected in a filter and washed with water (Dumas). In this process, however, a considerable quantity of the oxamide is decomposed by the heat. Hence it is more advantageous to prepare it by the action of ammonia on oxalic ether (p. 269). For this purpose aqueous ammonia is mixed with oxalic ether, either pure or dissolved in alcohol, and the precipitated oxamide is washed with water and alcohol (Bauhof and Liebig). Or the distillate obtained from 1 pt. of salt of sorrel, 1 pt. alcohol, and 2 pts. oil of vitriol, may be immediately shaken up with aqueous ammonia. The clear mixture becomes heated and deposits oxamide, which must be washed first with water and then with alcohol. (Liebig.)

Oxamide is also formed from cyanogen and cyanides. Playfair found it amongst the products of the action of nitric acid on ferrocyanide of potassium (ii. 251).

mixed with aldehyde gradually deposits crystals of oxamide, the whole of the cyanogen being thereby converted into oxamide, while the aldehyde appears to undergo no alteration, as the solution, if again saturated with cyanogen, yields an additional quantity of oxamide. An aqueous solution of hydrocyanic acid, mixed with peroxide of hydrogen, gradually yields a crystalline deposit of oxamide: $2CNH + H^2O^2 = C^2H^4N^2O^2$. Oxamide is also formed when a mixture of potassium-cyanide and manganic peroxide is heated with a small quantity of sulphuric acid. (Attfield, Chem. Soc. J. xvi. 94.)

A small quantity of oxamide appears to be sometimes formed by the action of nitric acid upon acetone. (Riche, Jahresb. 1859, p. 340.)

*Properties.*—Oxamide is a light white powder, tasteless, odourless, and insoluble in cold water. Boiling *water* dissolves it in small quantity, and deposits it on cooling in crystalline flocks. The solution is neutral to test-papers, and does not precipitate calcium salts. Oxamide is insoluble in *alcohol*.

*Decompositions.*—1. Oxamide heated in an open tube volatilises and forms a confusedly crystalline sublimate; heated in a retort it decomposes partially, leaving a residue of charcoal. The vapour passed through a red-hot glass tube 2 feet long, is completely resolved, without deposition of carbon, into carbonic oxide, carbonate of ammonium, hydrocyanic acid, and urea (Liebig):

$$\underset{\text{Oxamide.}}{2C^2H^4N^2O^2} = CO + CO^2 + NH^3 + CNH + \underset{\text{Urea.}}{CH^4N^2O}.$$

But when hermetically sealed in a metal tube (which conducts the heat well) and heated for some minutes to 310°, it is partially decomposed, yielding cyanogen, carbonic anhydride, and ammonia (Malaguti). The first products are probably cyanogen and water:

$$C^2H^4N^2O^2 = 2CN + 2H^2O;$$

but the water, acting at 200° on another portion of the oxamide, forms oxalate of ammonium:

$$C^2H^4N^2O^2 + 2H^2O = C^2(NH^4)^2O^4;$$

and the oxalate of ammonium is resolved at 220° into ammonia, carbonic anhydride, and carbonic oxide. Similarly, a mixture of oxamide and sand, heated in a retort to 300°—330°, yields nothing but cyanogen, carbonic oxide, and carbonate of ammonium. (Malaguti.)

2. Heated with *phosphoric anhydride*, it yields a large quantity of cyanogen, together with carbonic anhydride and carbonic oxide. (Bertagnini, Ann. Ch. Pharm. civ. 176.)

3. Oxamide, kept in contact for some time with saturated *chlorine-water*, disappears completely, forming hydrochloric acid, oxalic acid, and probably also chloride of nitrogen, which then undergoes further decomposition, but without formation of sal-ammoniac. (Malaguti.)

4. Oxamide, boiled with a fourfold quantity of *nitric acid*, of specific gravity 1·35, is resolved into a mixture of 1 vol. nitrogen, 1 vol. nitrous oxide, and 2 vol. carbonic anhydride (Malaguti):

$$C^2H^4N^2O^2 + 2HNO^3 = N^2 + N^2O + 2CO^2 + 3H^2O.$$

According to Bauhof, nitric acid, even when hot, has no action upon oxamide; according to O. Henry and Plisson, strong nitric acid forms with it ammonia and carbonic anhydride.

5. With strong *sulphuric acid*, but only when heated, oxamide forms carbonic oxide and carbonic anhydride in equal volumes, ammonia remaining behind in combination with the sulphuric acid, which remains colourless (Dumas, Liebig):

$$C^2H^4N^2O^2 + H^2O = CO + CO^2 + 2NH^3.$$

6. All the stronger acids in the dilute state decompose oxamide, yielding an ammonium-salt and free oxalic acid. (O. Henry and Plisson.)

$$C^2H^4N^2O^2 + H^2SO^4 + H^2O = (NH^4)^2SO^4 + C^2H^2O^4.$$

Such is the action exerted by sulphuric, hydrochloric, nitric, and tartaric acid, as well as by oxalic acid itself; but not by acetic acid, which indeed, when boiled with oxamide, goes off in vapour without exerting any action. (O. Henry and Plisson.)

7. Oxamide is not altered by fourteen days' contact with cold *water*, or by boiling with water; but when heated with water to 224° under increased pressure, it yields a liquid, which is acid after evaporation, gives off ammonia with hydrated oxide of lead, and yields an abundant precipitate with calcium-salts. (O. Henry and Plisson.)

8. Oxamide, heated with aqueous *alkalis*, is resolved into alkaline oxalate and ammonia, which volatilises, without any trace of alcohol (Dumas):

$$C^2H^4N^2O^2 + 2KHO = C^2K^2O^4 + 2NH^3.$$

Aqueous *ammonia* decomposes oxamide, even at ordinary temperatures, gradually dissolving it in the same manner (O. Henry and Plisson). By continued boiling with aqueous ammonia, oxamide is converted into oxamic acid (Toussaint, p. 279). Boiling *carbonate of potassium*, according to Bauhof, has no action upon oxamide.

The boiling aqueous solution of oxamide does not precipitate *nitrate or acetate of lead;* but on the addition of a small quantity of ammonia, and application of heat, it throws down basic oxalate of lead; the decomposition of oxamide into oxalic acid and ammonia takes place much more quickly under these circumstances than under the influence of acids or alkalis alone, being assisted probably by the insolubility of the lead-salt. (Pelouze.)

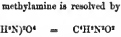
9. On gently heating oxamide in contact with *potassium*, cyanide of potassium is formed with vivid deflagration (Liebig)—probably thus:

$$C^2H^4N^2O^2 + K^4 = 2CNK + 2KHO + H^2.$$

10. When oxamide is boiled with water, and *mercuric oxide* is gradually added, a compound of the bodies containing $2C^2H^4N^2O^2.Hg''O$ separates as a white powder (Dessaignes). But dry oxamide heated with mercuric oxide, is oxidised, yielding urea and carbonic anhydride (Williamson):

$$C^2H^4N^2O^2 + Hg''O = CH^4N^2O + CO^2 + Hg.$$

*Oxamides containing Alcohol-radicles.*

**Dimethyloxamide.** 
$C^4H^8NO^2 = \left.\begin{matrix}(C^2O^2)''\\(CH^3)^2\\H^2\end{matrix}\right\}N^2$ (Wurtz, Ann. Ch. Phys. [3] **xxx.** 464).—Neutral oxalate of methylamine is resolved by dry distillation into water and dimethyloxamide:

$$C^2(CH^6N)^2O^4 = C^4H^8N^2O^2 + 2H^2O.$$

The transformation is much more complete than that of oxalate of ammonium into oxamide, because dimethyloxamide is much more volatile than oxamide. The dimethyloxamide collects in the neck of the retort in the form of long delicate needles interlacing each other in all directions.

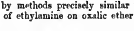
The compound is also produced by the action of a solution of methylamine on oxalic ether, the products being alcohol and dimethyloxamide:

$$C^2(C^2H^5)^2O^4 + 2CH^5N = 2C^2H^6O + C^4H^8N^2O^2.$$

This is the better mode of preparation. The reaction takes place immediately, with evolution of heat, the product being a white magma composed of delicate needles; these dissolve readily in hot water, and, as the solution cools, the dimethyloxamide crystallises in the form of long interlaced needles. It dissolves in alcohol less readily than in water. The fixed alkalis decompose it easily, with evolution of methylamine and formation of an alkaline oxalate:

$$C^4H^8N^2O^2 + 2KHO = C^2K^2O^4 + 2CH^5N.$$

It is carbonised by phosphoric anhydride.

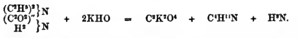
**Diethyloxamide.** 
$C^6H^{12}N^2O^2 = \left.\begin{matrix}(C^2O^2)''\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2$ (Wurtz, Ann. Ch. Phys. [3] **xxx.** 490).—Obtained by methods precisely similar to those which yield dimethyloxamide; the reaction of ethylamine on oxalic ether affords the best mode of preparation.

Diethyloxamide is more soluble in alcohol and water than oxamide. From the alcoholic solution it crystallises in beautiful needles. It is volatile, and condenses on the surface of cold bodies in woolly crystals. Potash decomposes it, forming ethylamine and oxalate of potassium:

$$C^6H^{12}N^2O^2 + 2KHO = C^2K^2O^4 + 2C^2H^7N.$$

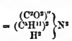
Phosphoric anhydride carbonises it.

Hofmann, by acting on ethylic diethyloxamate (p. 281) with ammonia, obtained a compound metameric with that just described, but differing from it in the mode of its decomposition by alkalis, yielding, not 2 at. methylamine, but 1 at. diethylamine and 1 at. ammonia. It may, in fact, be regarded as consisting of a molecule of diethylamine and a molecule of ammonia, bound together by the diatomic radicle oxalyl:



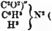
$$\left.\begin{matrix}(C^2H^5)^2\end{matrix}\right\}N \atop \left.\begin{matrix}(C^2O^2)''\\H^2\end{matrix}\right\}N \quad + \quad 2KHO \quad = \quad C^2K^2O^4 \quad + \quad C^4H^{11}N \quad + \quad H^3N.$$

Wnrtz's diethyloxamide, on the other hand, consists of 2 at. ethylamine bound together in a similar manner.

**Diamyloxamide.** $C^{12}H^{24}N^2O^2$ =  $\left.\begin{matrix}(C^2O^2)''\\(C^5H^{11})^2\\H^2\end{matrix}\right\}N^2$ (Wurtz, *loc. cit.*).—Obtained hy heating ethylic oxalate with amylamine. It solidifies to a mass of silky needles, melting at 139°, and perfectly volatile. It is insolnhle in water, hnt dissolves in hot alcohol, from which it separates almost wholly on cooling.

**Naphthyl-oxamides.** *a.* DINAPHTHYL-OXAMIDE. *Oxanaphthalide.* $C^{22}H^{16}N^2O^2$ = $\left.\begin{matrix}(C^{10}H^7)^2\\(C^2O^2)''\\H^2\end{matrix}\right\}N^2$ (Zinin, Ann. Ch. Pharm. cviii. 22).—Prodnced, together with naphthyl-formamide, by the action of heat on nentral or acid oxalate of naphthylamine. (For the mode of formation and preparation, see ii. 681.) It forms small scales insolnhle in water, sparingly soluble in boiling alcohol, melting at abont 200°. When heated above its melting point, it is gradnally decomposed, giving off carbonic oxide and leaving dinaphthylcarbamide. When boiled with *alcoholic potash*, or heated with very strong *aqueous potash*, it is resolved into naphthylamine and oxalic acid.

*β.* CYANO-DINAPHTHYLOXAMIDE. *Menaphthoximide.* $C^{23}H^{15}N^3O^2$ = $\left.\begin{matrix}(C^{10}H^7)^2\\(C^2O^2)''\\CN\\H\end{matrix}\right\}N^3$ (Perkin, Chem. Soc. Qn. J. ix. 8). This compound, which has the composition of acid oxalate of menaphthylamine *minus* 2 at. water ($C^{21}H^{17}N^3.C^2H^2O^4 - 2H^2O = C^{23}H^{15}N^3O^2$). is deposited from an alcoholic solution of dicyanide of menaphthylamine (p. 24) mixed with hydrochloric acid and left at rest, in small yellow spangles insolnhle in *water*, very slightly solnhle in *alcohol* and *ether*. It melts at 245°, and decomposes at 260°, emitting white vapours probably containing cyanate of naphthyl. By aqueous *potash* and by *acids*, it is resolved into oxalic acid and menaphthylamine.

**Phenyloxamides.** *a.* MONOPHENYLOXAMIDE OR OXANILAMIDE, $C^8H^8N^2O^2$ =  $\left.\begin{matrix}(C^2O^2)''\\C^6H^5\\H^3\end{matrix}\right\}N^2$ (A. W. Hofmann, Ann. Ch. Pharm. lxxiii. 181).—This body is found among the prodncts of the decomposition of cyaniline hy hydrochloric acid. To prepare it, a solntion of cyaniline in dilnte hydrochloric acid is evaporated; the white crystalline mass is freed from sal-ammoniac and hydrochlorate of aniline hy digestion in cold water; the residne well boiled with water; the solntion evaporated to dryness after being filtered from diphenyloxamide; and the residne exhausted by boiling with alcohol. The alcoholic solntion, when cooled or evaporated, deposits the monophenyloxamide, which may be purified hy recrystallisation from hot water. The compound is not obtained by treating oxamethane with aniline.

Phenyloxamide forms snow-white, silky, capillary flakes, which sublime in the form of a soft powder. It is solnble in *alcohol* and *ether*, and crystallises from boiling *water*.

Strong *sulphuric acid* eliminates carbonic oxide and carbonic acid from it, and leaves sulphate of ammonium together with sulphanilic acid:

$$2C^8H^8N^2O^2 + 3H^2SO^4 = 2CO + 2CO^2 + (C^6NH^7)^2S^2O^6 + (NH^4)^2SO^4.$$

The originally transparent solntion in strong *potash-ley*, from which acids throw down the phenyloxamide nnaltered, becomes gradually clouded with drops of aniline, the more qnickly as it is stronger and warmer, then gives off ammonia, and forms oxalate of potassium:

$$C^8H^8N^2O^2 \quad + \quad 2KHO \quad = \quad C^6H^7N \quad + \quad NH^3 \quad + \quad C^2K^2O^4.$$

*β.* DIPHENYLOXAMIDE OR OXANILIDE, $C^{14}H^{12}N^2O^2$ = $\left.\begin{matrix}(C^2O^2)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2$ (Gerhardt, Ann. Ch. Phys. [3] xiv. 120; xv. 88;—J. Pharm. [3] ix. 406;—Hofmann, Ann. Ch. Pharm. lxv. 56; lxxiii. 181; lxxiv. 35).—This compound is formed: 1. Together with phenyl-formamide by heating oxalate of aniline to between 160° and 180°:

$$\underset{\text{Oxalate of aniline.}}{(C^6H^7N)^2.C^2H^2O^4} = \underset{\text{Diphenyloxamide.}}{C^{14}H^{12}N^2O^2} + 2H^2O.$$

$$(C^6H^7N)^2C^2H^2O^4 = \underset{\text{Phenylformamide.}}{C^7H^7NO} + C^6H^7N + CO^2 + H^2O.$$

The application of heat must be continued till the evolution of gas ceases, and the solidified mass exhausted with alcohol, which dissolves the phenylformamide, and leaves the diphenyloxamide. (Gerhardt.)

2. Together with oxamide and monophenyloxamide, in the decomposition of cyaniline by dilute hydrochloric or sulphuric acid:

$$\underset{\text{Cyaniline.}}{4C^{14}H^{14}N^4} + 8H^2O + 8HCl = 4NH^4Cl + \underset{\text{Hydrochlorate of aniline.}}{4C^6H^8NCl} + \underset{\text{Oxamide.}}{C^2H^4N^2O^2}$$
$$+ \underset{\text{Phenyloxamide.}}{2C^8H^8N^2O^2} + \underset{\text{Diphenyloxamide.}}{C^{14}H^{12}N^2O^2}$$

The solution of cyaniline in excess of dilute hydrochloric acid is evaporated over the water-bath; the dry residue treated with cold water to remove sal-ammoniac and hydrochlorate of aniline, then with boiling water, to dissolve oxamide and monophenyloxamide; and the diphenyloxamide which remains undissolved is purified by solution in benzene, filtration, and evaporation, and by washing the crystals with alcohol. (Hofmann.)

*Properties.*—Diphenyloxamide crystallises in white nacreous scales, which melt at 245°, and solidify in a radiating mass on cooling. It boils at 320°, giving off a sharp vapour like that of benzoic and distilling for the most part without decomposition, and sublimes at a gentle heat in iridescent laminæ. It does not dissolve in water or in dilute sulphuric acid, even at the boiling heat, but dissolves in slightly heated *strong sulphuric acid;* and is precipitated therefrom without alteration by water. It is insoluble in cold, sparingly soluble in boiling *alcohol*, more soluble in *benzene*, insoluble in *ether*.

*Decompositions.*—1. Diphenyloxamide subjected to rapid *distillation* yields a small quantity of oil containing a trace of anilocyanic acid, which gives it a powerful odour. —2. *Bromine* acts violently upon diphenyloxamide, giving off hydrobromic acid, and forming a substance which dissolves in ether and crystallises therefrom (Gerhardt). —3. Hot *nitric acid* gives off red vapours (Gerhardt). Aqueous *chromic acid* and other dilute acids do not act upon it, even when heated.—The solution of diphenyloxamide in warm *oil of vitriol* effervesces when strongly heated, giving off carbonic oxide and carbonic anhydride in equal volumes; it then turns slightly brown, and, on the addition of a small quantity of water, deposits a large quantity of anilosulphuric acid in the form of a white crystalline powder (Gerhardt):

$$C^{14}H^{12}N^2O^2 + 2H^2SO^4 = (C^6H^7N)^2S^2O^6 + CO + CO^2 + H^2O.$$

5. Diphenyloxamide *distilled* with phosphoric anhydride or chloride of zinc, gives off carbonic oxide and carbonic anhydride, and is almost completely carbonised; nevertheless, especially with phosphoric anhydride, the oil which smells of anilocyanic acid passes over, together with sublimed diphenylcarbamide, in larger quantity than when the diphenyloxamide is distilled alone (Hofmann).—6. Vapour of diphenyloxamide passed over red-hot *lime* yields a body which may be regarded as $C^{14}H^8N^2$ (Hofmann).—7. Diphenyloxamide heated with dry *lime* gives off aniline, and becomes partially carbonised, and sometimes heated to redness (Gerhardt). Anhydrous *baryta* eliminates scarcely anything but aniline (Hofmann). Diphenyloxamide heated with *potash-lime, hydrate of potassium*, or concentrated (not with dilute) *potash-ley*, is resolved into a distillate of aniline and a residue of oxalate of potassium. (Gerhardt.)

γ. CYANO-DIPHENYLOXAMIDE OR MELANOXIMIDE, $C^{15}H^{11}N^3O^2 = \left.\begin{matrix}(C^6H^5)^2\\(C^2O^2)''\\CN\\H\end{matrix}\right\}N^2$

(Hofmann, Chem. Soc. Qu. J. ii. 307).—This compound, which has the composition of oxalate of melaniline *minus* 2 at. water, is formed in the decomposition of dicyanomelaniline by acids:

$$C^{15}H^{13}N^5 + 2HCl + 2H^2O = C^{15}H^{11}N^3O^2 + 2NH^4Cl.$$

To prepare it, dicyanomelaniline is dissolved in moderately strong hydrochloric acid, and the gradually precipitated crystalline powder (or slowly crystallising resin) washed with water. It is a pale yellow indistinctly crystalline powder, insoluble in *water* and in aqueous *acids*, sparingly soluble in boiling *alcohol*, whence it crystallises in crusts. In aqueous *ammonia* or *potash* it dissolves at first without decomposition, and may be precipitated from the solution by acids; afterwards decomposition takes place. Its solution in weak alcohol forms, with nitrate of *silver*, especially on addition of a small quantity of ammonia, a light yellow amorphous precipitate, containing from 25·4 to 28·57 and 30·5 per cent. of silver.

*Decompositions.*—1. Melanoximide melts when *heated*, giving off a large quantity of carbonic oxide, together with a small quantity of carbonic anhydride (probably resulting from a secondary decomposition), and with the strong-smelling vapour of anilocyanic acid, about 10 per cent. of which condenses in the form of a yellowish liquid; at a stronger heat, the melanoximide ultimately yields diphenylcarbamide sublimed in radiating crystals, and leaves a pale yellow transparent mass of resin.—2. Melanoximide is but slightly decomposed by dilute *sulphuric* or *hydrochloric acid;* but when dissolved in alcohol and boiled with concentrated hydrochloric acid, it is resolved into oxalic acid, melaniline, and needles not yet fully examined, the solution at the same time acquiring a deep yellow colour, and emitting a powerful odour of anilocyanic acid.—3. Its alcoholic solution solidifies in contact with *ammonia* or *potash*, either of which takes up a large quantity of oxalic acid, forming crystals of melaniline; and a similar decomposition takes place gradually in its solution in aqueous ammonia or potash, especially when concentrated.

**OXANAPHTHALIDE.** Syn. with Dinaphthyloxamide (p. 285).

**OXANILAMIDE.** Syn. with Phenyloxamide (p. 285).

**OXANILIC ACID.** Syn. with Phenyloxamic Acid (p. 281).

**OXANILIDE.** Syn. with Diphenyloxamide (p. 285).

**OXANILINE.** $C^6H^7NO$ (R. Schmidt, Chem. Soc. J. xvii. 194).—A base produced, together with other bodies, by the action of heat on amido-salicylic acid:

$$C^7H^7NO^3 = C^6H^7NO + CO^2.$$

To obtain it, amido-salicylic acid is heated with pumice-stone, and the resulting sublimate is treated with alcohol slightly acidulated with acetic acid; oxaniline then remains in the form of a white inodorous mass. It dissolves in hot water and hot alcohol, and separates on cooling in slightly coloured crystals.

The aqueous solution turns brown in the air, and deposits a brown amorphous substance. It easily reduces the solutions of the noble metals, acquiring at the same time a splendid violet colour, which is also imparted to it by nitric acid. When mixed with an alkaline liquid, it acquires a deep indigo-blue colour, which disappears on addition of an acid.

Oxaniline unites readily with hydrochloric, hydrobromic, hydriodic, sulphuric acid, &c., forming soluble crystallisable salts. The solutions decompose in contact with the air, if they are perfectly neutral, but are stable when acid.

**OXANTHRACENE.** See Paranaphthalene.

**OXATOLYLIC ACID.** $C^{16}H^{16}O^3$. (Möller and Strecker, Ann. Ch. Pharm. cxiii. 56.)—An acid produced, together with methylic alcohol, by boiling vulpic acid with potash-ley of specific gravity 1·05 to 1·15:

$$\underset{\text{Vulpic acid.}}{C^{19}H^{14}O^5} + 3H^2O = \underset{\text{Oxatolylic acid.}}{C^{16}H^{16}O^3} + \underset{\text{Methylic alcohol.}}{CH^4O} + 2CO^2.$$

When the decomposition is complete, which may be known by the change of colour of the precipitate from yellow to a faint dingy tint, the oxatolylic acid may be precipitated by hydrochloric acid. It crystallises from alcohol in colourless, brittle, right rhombic, four-sided prisms, terminated by domes. It melts at 154°, volatilises with decomposition at a higher temperature, is sparingly soluble in hot water, easily in alcohol and ether. It has a strong acid reaction, and forms easily soluble salts with the alkalis, sparingly soluble with the alkaline earths. The *barium-salt*, $C^{32}H^{30}Ba''O^6.4H^2O$, the *silver-salt*, $C^{16}H^{15}AgO^3$, and the *lead-salt*, $C^{32}H^{30}Pb''O^6.4H^2O$, are crystalline precipitates; the *ethylic ether*, $C^{16}H^{15}(C^2H^5)O^3$, prepared by saturating the alcoholic solution of the acid with hydrochloric acid and heating, or more easily by treating the silver-salt with ethylic iodide, forms colourless prismatic crystals, which melt at 45·5°.

Oxatolylic acid, boiled with *potash-ley* of specific gravity 1·2 to 1·3, is resolved into oxalic acid and hydride of benzyl (toluene), $C^7H^8$, which distils over:

$$C^{16}H^{16}O^3 + H^2O = C^2H^2O^4 + 2C^7H^8.$$

It dissolves in *fuming nitric acid*, forming nitro-oxatolylic acid, $C^{16}H^{15}(NO^2)O^3$, which is resolved with greater facility by boiling potash into oxalic acid and hydride of nitrobenzyl.

**OXETHYL.** This name is applied to peroxide of ethyl, $C^2H^5O$, entering into combination as a monatomic radicle. (See ETHYLENE-BASES, ii. 593, and PHOSPHORUS-BASES.)

Lieben (Ann. Ch. Pharm. cxxxiii. 287), by treating the chlorinated derivatives of ethylic oxide, $(C^2H^5)^2O$, with ethylate of sodium or alcoholic potash, has obtained compounds consisting of ethylic oxide, in which 1 or 2 at. hydrogen is replaced by oxethyl.

*a. Oxethyl-chlorethylic oxide,* $\left.\begin{matrix}C^2H^4Cl\\ C^2H^4(C^2H^5O)\end{matrix}\right\}O$.—This compound is obtained by treating dichlorethylic oxide with an alcoholic solution of sodium:

$$\left.\begin{matrix}C^2H^4Cl\\ C^2H^4Cl\end{matrix}\right\}O \quad + \quad NaC^2H^5O \quad = \quad \left.\begin{matrix}C^2H^4Cl\\ C^2H^4(C^2H^5O)\end{matrix}\right\}O \quad + \quad NaCl.$$

The action begins at common temperatures, but requires the aid of a gentle heat to complete it. The alcoholic liquid is then to be mixed with a large quantity of water to dissolve out the chloride of sodium, and the oil which separates washed with water. Alcoholic potash acts in a similar manner, but gives rise at the same time to the formation of a considerable quantity of resinous products.

The oil obtained as above consists mainly of oxethyl-chlorethylic oxide, which is heavier than water, has a very agreeable refreshing odour, and boils at 159°. It is difficult, however, to obtain this compound pure, as, according to the greater or smaller quantity of sodium-ethylate employed, the product is contaminated either with dioxethyl-ethylic oxide (*vid. inf.*) or with dichlorethylic oxide. The latter may be removed by heating the oil to 100° with aqueous potash, but the remaining oil is still contaminated with a more highly chlorinated product.

*β. Dioxethylic oxide,* $\left.\begin{matrix}C^2H^4(C^2H^5O)\\ C^2H^4(C^2H^5O)\end{matrix}\right\}O$.—Obtained by heating dichlorethylic oxide in a sealed tube for some hours to about 140°, with excess of alcoholic potash or sodium-ethylate:

$$\left.\begin{matrix}C^2H^4Cl\\ C^2H^4Cl\end{matrix}\right\}O \quad + \quad 2NaC^2H^5O \quad = \quad \left.\begin{matrix}C^2H^4(C^2H^5O)\\ C^2H^4(C^2H^5O,)\end{matrix}\right\}O \quad + \quad 2NaCl.$$

The product is washed with water or solution of chloride of calcium, and dried over chloride of calcium. When thus purified it is lighter than water, and boils at about 168°.

*γ. Ethyl-oxethylic oxide,* $\left.\begin{matrix}C^2H^4(C^2H^5)\\ C^2H^4(C^2H^5O)\end{matrix}\right\}O$.—When ethyl-chlorethylic oxide $\left.\begin{matrix}C^2H^4(C^2H^5)\\ C^2H^4Cl\end{matrix}\right\}O$, the product obtained by the action of zinc-ethyl on dichlorethylic ether, is treated with sodium-ethylate or alcoholic potash, and the product treated with water as above, an oil is obtained consisting chiefly of ethyl-oxethylic oxide, together with a very small quantity of another compound boiling at 70°. The principal reaction is represented by the equation:

$$\left.\begin{matrix}C^2H^4(C^2H^5)\\ C^2H^4Cl\end{matrix}\right\}O \quad + \quad KC^2H^5O \quad = \quad \left.\begin{matrix}C^2H^4(C^2H^5)\\ C^2H^4(C^2H^5O)\end{matrix}\right\}O \quad + \quad KCl.$$

Ethyl-oxethylic oxide is an oil of ethereal odour, lighter than water, and boiling at 148°.

By using sodium-methylate instead of sodium-ethylate, and zinc-methyl instead of zinc-ethyl, a whole series of compounds might be obtained, homologous with those just described. (Lieben.)

**OXETHYLENE-BASES.** See ETHYLENE-BASES (ii. 593).

**OXETHYL-TRIETHYL-PHOSPHONIUM.** See PHOSPHORUS-BASES.

**OXHAVERITE.** Syn. with APOPHYLLITE (i. 357).

**OXIDATION.**
**OXIDES.** } See OXYGEN.

**OXINDICANIN.**
**OXINDICASIN.** } Products of the decomposition of indican (iii. 247).

**OXONIC ACID.** Syn. with GLYCOLLIC ACID. F. Schulze applied this name to the acid obtained by the action of nascent hydrogen on pure oxalic acid, supposing it to be a distinct acid (see ii. 910, No. 8).

**OXURIC ACID.** *White purpuric acid.*—These names were applied by Vauquelin to a product obtained by treating uric acid with nitric acid, and neutralising with lime; it appears, however, to have been merely a mixture of alloxan and alloxanic acid. (See *Gmelin's Handbook*, x. 169.)

**OXYACANTHIN.** A bitter neutral substance obtained by Leroy (Vierteljahrsschr. pr. Pharm. viii. 575) from the whitethorn (*Cratægus oxyacantha*).

**OXYACANTHINE.** $C^{32}H^{46}N^2O^{11}$? *Vineline.* (Polex, Arch. Pharm. vi. 265.—

Wacker, Jahresb. 1861, p. 545).—An alkaloïd existing, together with berberine, in the root of *Berberis vulgaris*. To extract it, the root is exhausted with alcohol, a little water is added to the extract, and the alcohol is distilled off. The remaining liquid deposits a resin, which must be separated by filtration, and the filtrate when concentrated deposits crystals of berberine. When the mother-liquors no longer yield this base, they are to be diluted with four measures of water and precipitated by carbonate of sodium, the precipitate washed with cold water and dissolved in dilute sulphuric acid, the solution decolorised with animal charcoal, and the oxyacanthine again precipitated by carbonate of sodium. (Polex.)

Oxyacanthine, when pure, is a white powder ordinarily with a yellowish tinge. It may be obtained in the crystalline state by spontaneous evaporation of its alcoholic solution mixed with a quantity of water not sufficient to render it turbid. It has a bitter taste, turns brown on exposure to air and light, melts when heated, and gives off water, empyreumatic vapours, and ammonia, leaving a carbonaceous residue (Polex). It melts at 139°, and decomposes at a higher temperature (Wacker). It is nearly insoluble in cold water, but when recently precipitated it dissolves in a small quantity of boiling water. It is soluble in alcohol, ether, and oils both fixed and volatile: its solutions have an alkaline reaction (Polex). According to Wacker, it dissolves in 30 pts. of cold alcohol, and in its own weight of boiling alcohol of 90 per cent.; in 125 pts. cold and 4 pts. warm ether, also in chloroform. When precipitated by ammonia from its salts, it dissolves in a large excess of ammonia, much more easily in caustic potash, not in alkaline carbonates.

Oxyacanthine is decomposed by mineral acids. Nitric acid when boiled with it first resinises it, and then converts it into oxalic acid and a body resembling berberine, which is precipitated in yellow flocks by water (Polex). With iodic acid and a small quantity of water, it separates iodine, assuming a yellow or brown colour. (Wacker.)

Air-dried oxyacanthine has, according to Wacker, the composition $C^{32}H^{46}N^2O^{11}.H^2O$.

The salts have a bitter taste (Polex). The *hydrochlorate*, $C^{32}H^{46}N^2O^{11}.2HCl.4H^2O$, crystallises in white nodules; so likewise the *sulphate*, and the less soluble *nitrate*, which contains 4 at. water. The *oxalate* crystallises in sparingly soluble needles; the *acetate* is uncrystallisable. (Wacker.)

The neutral solution of the acetate gives a white precipitate with tincture of galls, nitrate of silver, mercuric chloride, tartar-emetic, and stannous chloride; brown-red with iodine; yellow with platinic chloride and picric acid: it is not precipitated by mercurous nitrate, ferric chloride, neutral or basic acetate of lead, copper-salts or gelatin. (Polex.)

**OXYANISAMIC ACID.** $C^8H^9NO^3 = \left.\begin{matrix}H^2\\(C^8H^5O)'''\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$.—Already described as an anisamic acid (i. 296).—The rational formula just given represents it as derived from a triatomic and monobasic oxyanisic acid, $C^8H^8O^4 = \left.\begin{matrix}H^3\\(C^8H^5O)'''\\H\end{matrix}\right\}O^3$. It may also be regarded as amido-anisic acid, $C^8H^7(NH^2)O^3$.

**Diazoanis-oxyaniasmic Acid,** or *Diazoanisamidanisic acid*, $C^{16}H^{15}N^3O^6 = C^8H^6N^2O^3.C^8H^9NO^3$. (P. Griess, Ann. Ch. Pharm. cxiii. 337; cxvii. 44; Jahresb. 1859, p. 467; 1861, p. 414).—An acid produced by the action of nitrous acid or a nitrous ether on an alcoholic solution of oxyanisamic acid:

$$2C^8H^9NO^3 + NHO^2 = C^{16}H^{15}N^3O^6 + 2H^2O.$$

The reaction must take place at a rather low temperature, and all excess of nitrous acid must be avoided.

Diazoanis-oxyanisamic acid is a yellow or greenish-yellow amorphous substance, analogous in its properties and reactions to diazobenzo-oxybenzamic acid (p. 291). It may be regarded either as formed from a double molecule of oxyanisamic acid by the substitution of 1 at. nitrogen for 3 at. hydrogen, and represented by the formula $C^{16}(H^{15}N''')N^2O^6$, or according to Griess, as a compound of diazoanisic acid (*i.e.* anisic acid, $C^8H^8O^3$, in which 2 atoms of hydrogen are replaced by 2 atoms of nitrogen), with amido-anisic acid (*i.e.* anisic acid in which 1 at. hydrogen is replaced by amidogen, $NH^2$), that is as $C^8H^6N^2O^3.C^8H^7(NH^2)O^3$.

The reactions of diazoanis-oxyanisamic acid are similar to those of diazbenzo-oxybenzamic acid. With *hydrochloric acid* it gives off nitrogen and forms hydrochlorate of oxyanisamic acid, which remains dissolved, and a red amorphous powder $C^{16}H^{14}O^7$, which, when purified, exhibits the characters of an acid:

$$2C^{16}H^{15}N^3O^6 + 2HCl + H^2O = 2(C^8H^9NO^3.HCl) + C^{16}H^{14}O^7 + N^4.$$

Ethylic diazoanis-oxyanisamate (*vid. inf.*) behaves with hydrochloric acid in a similar manner. Chloranisic acid is never formed in this reaction; neither is bromanisic acid produced by the action of hydrobromic acid on diazoanis-oxyanisamic acid. *Hydriodic acid*, on the contrary, forms iodanisic acid and hydriodate of oxyanisic acid:

$$\mathrm{C^{16}H^{15}N^3O^6 \quad + \quad 2HI \quad = \quad C^8H^7IO^3 \quad + \quad C^8H^9NO^3.HI \quad + \quad N^2.}$$

The iodanisic acid separates as a reddish crystalline mass, and when purified forms small needles easily soluble in alcohol and ether, nearly insoluble in water. The hydrochlorate of oxyanisamic acid which remains in solution, may be obtained in stellate groups of laminæ and needles.

Diazoanis-oxyanisamic acid suspended in boiling alcohol is decomposed by nitrous acid, with evolution of nitrogen and formation of anisic acid and acetic aldehyde:

$$\underset{\text{Diazoanis-oxyanisamic acid.}}{\mathrm{C^{16}H^{15}N^3O^6}} + \underset{\text{Nitrous acid.}}{\mathrm{HNO^2}} + \underset{\text{Alcohol.}}{\mathrm{2C^2H^6O}} = \underset{\text{Anisic acid.}}{\mathrm{2C^8H^8O^3}} + \underset{\text{Aldehyde.}}{\mathrm{2C^2H^4O}} + \mathrm{2H^2O} + \mathrm{N^4}.$$

Alkalis decompose diazoanis-oxyanisamic acid, forming oxyanisamic acid and the above-mentioned red body $\mathrm{C^{16}H^{14}O^4}$.

The diazoanis-oxyanisamates, $\mathrm{C^{16}H^{13}M^2N^3O^6}$ or $\mathrm{C^{16}H^{13}M''N^3O^6}$ (according to the atomicity of the metal), are very unstable in solution, but when dry they can bear a heat above 160° without decomposition. The alkali-metal-salts are soluble in water; the rest are yellow or greenish-yellow precipitates.

The *ammonium-salt* forms golden-yellow laminæ, and decomposes rapidly when its aqueous solution is boiled. The *potassium-salt*, $\mathrm{C^{16}H^{13}K^2N^3O^6.2H^2O}$, forms golden-yellow laminæ which give off three-fourths of their water at 120°, the remainder at about 160°; at 180° the salt decomposes with slight detonation. The *sodium-salt*, $\mathrm{2C^{16}H^{13}Na^2N^3O^6.3H^2O}$, crystallises in golden-yellow six-sided tablets. The *magnesium-salt* forms greenish-yellow crystals sparingly soluble in water.

The *ethers* of diazoanis-oxyanisamic acid are prepared by passing nitrous acid vapour into alcoholic solutions of the corresponding oxyanisamic ethers. The *ethylic ether* is easily soluble in hot alcohol, whence it crystallises on cooling in narrow yellow-red laminæ; it is likewise soluble in ether, but insoluble in water. The *methylic ether* is exactly similar.

**OXYBENZAMIC ACID.** $\mathrm{C^7H^7NO^2} = \left.\begin{matrix}\mathrm{H^2}\\ \mathrm{(C^7H^4O)''}\\ \mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\ \mathrm{O}\end{matrix}.$ *Benzamic acid, Amidobenzoic acid.* (Zinin, J. pr. Chem. xxxvi. 103.—Chancel, Compt. rend. xxviii. 422.—Gerland, Ann. Ch. Pharm. lxxxvi. 143; xci. 185.—Voit, *ibid.* xcix. 100.)—This acid, the amic acid of oxybenzoic acid $\mathrm{C^7H^6O^3}$, was formerly called *Benzamic acid;* but the denomination is improper since benzoic acid is monobasic and cannot form an amic acid (i. 165). It may also be regarded as *amidobenzoic* acid $\mathrm{C^7H^5(NH^2)O^2}$, that is as benzoic acid in which 1 at. hydrogen is replaced by amidogen. It is metameric with phenyl-carbamic acid, $\left.\begin{matrix}\mathrm{H.C^6H^5}\\ \mathrm{(CO)''}\\ \mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\ \mathrm{O}\end{matrix}.$

It is best prepared by dissolving nitrobenzoic acid in aqueous ammonia, and saturating the boiling solution with sulphuretted hydrogen, air being excluded as far as possible. The liquid is decanted from the separated sulphur, and neutralised with acetic acid, when it deposits crystals of oxybenzamic acid, which are purified by recrystallisation from water (Gerland). Schiff (Ann. Ch. Pharm. ci. 94) obtains it by digesting nitrobenzoic acid with iron-filings and acetic acid. Chancel obtains it by boiling oxybenzodiamide with strong potash until ammonia ceases to escape, and super-saturating the liquid with acetic acid. The following are the reactions:

$$\underset{\text{Nitrobenzoic acid.}}{\mathrm{C^7H^5NO^4}} \quad + \quad \mathrm{3H^2S} \quad = \quad \underset{\text{Oxybenzamic acid.}}{\mathrm{C^7H^7NO^2}} \quad + \quad \mathrm{2H^2O} \quad + \quad \mathrm{S^3}$$

$$\underset{\text{Oxybenzodiamide.}}{\mathrm{C^7H^8N^2O}} \quad + \quad \mathrm{KHO} \quad = \quad \underset{\text{Potassic Oxybenzamate.}}{\mathrm{C^7H^6KNO^2}} \quad + \quad \mathrm{NH^3}$$

Oxybenzamic acid forms white crystalline nodules, or transparent needles, according as its aqueous solution is evaporated rapidly or slowly. It has a sweetish-sour taste, and reddens litmus strongly; is sparingly soluble in cold *water;* readily in boiling water, *alcohol* or *ether*. Its solution decomposes by exposure to the air, and yields a brown resinous substance. When heated, it melts, gives off irritating vapours, and leaves an abundant residue of carbon. Heated with *spongy platinum*, it is decomposed into aniline and carbonic acid. Heated with *solid potash*, it gives off empyreumatic vapours containing ammonia, but no aniline: under the same circumstances phenylcarbamic acid yields aniline abundantly. Boiled with *fuming nitric acid*, it is converted into trinitrophenic (picric) acid. When *nitrous acid fumes* are passed into its aqueous solution, nitrogen is evolved, and a red amorphous precipitate formed, which redissolves if the action of the gas is prolonged: the solution yields on evaporation crystals of oxybenzoic acid. Nitrous acid passed into an alcoholic solution of oxybenzamic acid converts it into diazobenzoxybenzamic acid (*vid. inf.*); but when a solution of oxybenzamic acid in cold aqueous or alcoholic nitric acid is exposed to the action of nitrous acid, the product consists of nitrate of diazobenzoic acid, $C^7H^4N^2O^2.NHO^3$. (Griess, p. 293.)

Oxybenzamic acid is converted into benzoic acid by boiling with water and *peroxide of manganese*, or *permanganate of potassium*, and by *chlorine* (in an aqueous solution). In an alcoholic solution, chlorine produces a black resinous substance, insoluble in water, soluble in alcohol with violet colour. It is attacked by *potassic chromate* and *sulphuric acid*, carbonic anhydride being evolved.

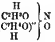
*Metallic Oxybenzamates.* $C^7H^6MO^2$.—These salts resemble the anthranilates very closely. The alkaline and alkaline-earthy salts are readily soluble in water and alcohol, and crystallise with difficulty. When heated with potash or lime they evolve carbonic anhydride, aniline, and ammonia. The *copper-salt* is a green precipitate, insoluble in water and alcohol, soluble in acids. There are three *lead-salts*; one, pulverulent and insoluble in water; another forming sparingly soluble needles; a third, more soluble, forming shining laminæ. The *silver-salt* is a white curdy precipitate, which soon becomes crystalline; in boiling water it becomes violet-brown, but does not dissolve; it is decomposed when heated above 100°.

*Oxy-benzamic ethers.* (Chancel, Compt. rend. xxx. 751.)—The only two known are the *oxybenzamate of methyl*, $C^7H^6(CH^3)NO^2$, and *of ethyl*, $C^7H^6(C^2H^5)NO^2$. They are obtained by the action of sulphide of ammonium on the corresponding nitrobenzoates; on the addition of water, they separate as heavy oily liquids, and are purified by repeated solution in alcohol and precipitation by water. Potash converts them into oxybenzamic acid and the corresponding alcohol; ammonia, into oxybenzodiamide and the corresponding alcohol:

$$\underset{\text{Oxybenzamate ethyl.}}{C^9H^{11}NO^2} \quad + \quad NH^3 \quad = \quad \underset{\text{Oxybenzodiamide.}}{C^7H^8N^2O} \quad + \quad C^2H^6O.$$

Like phenyl-carbamic acid, oxybenzamic acid combines directly with acids. The *hydrochlorate* of oxybenzamic acid, $C^7H^7NO^2.HCl$, separates in groups of needles, when hydrochloric acid is added to the liquid obtained by treating nitrobenzoic acid with sulphide of ammonium (Voit). With dichloride of platinum, it forms a yellow *chloroplatinate*, $2C^7H^7NO^2.H^2Cl^2.Pt^{iv}Cl^4$. The *nitrate*, $C^7H^7NO^2.NO^3H$, is formed when oxybenzamic acid is heated with nitric acid; the acid dissolves quietly, and crystals separate out on cooling, which are repeatedly crystallised from water. It forms thin laminæ, permanent in the air, and soluble in water and alcohol. The *sulphate*, $2(C^7H^7NO^2).SO^4H^2$, is formed when oxybenzamic acid is dissolved in strong sulphuric acid. Heat is evolved; and the mixture solidifies on cooling into a mass of shining crystals, which are purified by recrystallisation from hot water. It is permanent in the air, and has an intensely sweet taste. It is partly decomposed by hot water, sulphuric and oxybenzamic acids being formed; the same decomposition is effected by potash, by the carbonates of barium and lead, and by boiling with chloride of barium. (Gerland.)

F. T. C.



**Acetoxybenzamic Acid,** $C^9H^9NO^3 = \left.\begin{matrix} H \\ C^2H^3O \\ (C^7H^4O)'' \\ H \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$ (G. C. Foster, Chem. Soc. Qu. J. xiii. 235).—This acid, metameric with hippuric acid (benzoxacetamic acid,

$\left.\begin{matrix} H \\ C^7H^5O \\ (C^2H^2O)'' \\ H \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix}$, ii. 698; iii. 156), is produced: 1. By heating oxybenzamic acid with acetic acid to 130°—140° in a sealed tube:

$$C^7H^7NO^2 \quad + \quad C^2H^4O^2 \quad = \quad C^9H^9NO^3 \quad + \quad H^2O.$$

2. By the action of chloride of acetyl or acetic acid on oxybenzamate of zinc:

$$C^{14}H^{12}Zn''N^2O^4 \quad + \quad 2C^2H^3OCl \quad = \quad 2C^9H^9NO^3 \quad + \quad Zn''Cl^2.$$

The first process is the best. The product is dissolved in an alkali, precipitated with hydrochloric acid, and purified by recrystallisation, with aid of animal charcoal.

Acetoxybenzamic acid is a white powder consisting of microscopic crystals, nearly insoluble in cold *water* and *ether*, sparingly soluble in boiling water, easily in boiling *alcohol*. Like hippuric acid, it dissolves easily in ordinary *phosphate of sodium*, forming an acid solution from which it is precipitated by acetic acid and by mineral acids. With *strong sulphuric acid* and *glacial acetic acid*, it forms colourless solutions which are precipitated by water. With *hydrochloric* and *nitric acids* it appears to form solid but easily decomposible compounds. It sublimes at 200°, melts between 220° and 230°, and begins to boil at 260°. It is not decomposed by boiling with water or with dilute acids, but when heated with *hydrochloric* or *dilute sulphuric acid* to 140° in a sealed tube, it is resolved into acetic acid and (hydrochlorate or sulphate of) oxybenzamic acid, just as hippuric acid is resolved under similar circumstances into benzoic and oxyacetamic acid or glycocine (iii. 158):

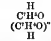
$$C^9H^9NO^3 \quad + \quad H^2O \quad = \quad C^2H^4O^2 \quad + \quad C^7H^7NO^3.$$

When treated with an alcoholic solution of hydrochloric acid, it yields, slowly in the cold, more quickly at 100°, oxybenzamate and acetate of ethyl, together with the free acids. When *nitrous acid* is passed into a boiling solution of acetoxybenzamic acid, or when a mixture of the latter with nitric acid is treated with nitric oxide gas, nitro-compounds are produced, but no acetoxybenzoic acid.

*Acetoxybenzamates.*—The *potassium-* and *sodium-salts* are easily soluble in water and in alcohol, insoluble in ether, and difficult to crystallise. The *sodium-salt* dried at 120° has the composition $C^9H^8NaNO^3$. The *barium-salt*, $C^{18}H^{16}Ba''N^2O^6.3H^2O$, is also easily soluble and crystallises in slender needles. The *calcium-salt*, $C^{18}H^{16}Ca''N^2O^6.3H^2O$, is deposited from the hot solution in thin rhombic laminæ. The *lead-salt* is a white precipitate which melts in boiling water and gradually dissolves. Nitrate of *silver* and chloride of *zinc* do not precipitate moderately strong solutions of acetoxybenzamates.

*Ethylic oxybenzamate* appears to be obtained as an oily, gradually solidifying compound by heating acetoxybenzamic acid with alcohol to 150°.

**Benzoxybenzamic Acid**, $C^{14}H^{11}NO^3$ =



$$\left.\begin{matrix} H \\ C^7H^5O \\ (C^7H^4O)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O' \end{matrix}$$

appears to be produced by the action of chloride of benzoyl on oxybenzamate of zinc. The product, which is insoluble in ether, sparingly soluble in water and in alcohol, and resembles acetoxybenzamic acid in taste and in appearance under the microscope, is probably identical with the *glycobenzamic acid* which Cahours obtained (Ann. Ch. Pharm. ciii. 90) by treating oxybenzamate of silver with chloride of benzoyl. (Foster.)

**Diazobenzo-oxybenzamic** or **Diazobenzo-amidobenzoic Acid.** $C^{14}H^{11}N^3O^4 = C^7H^4N^2O^2.C^7H^7NO^2$. (P. Griess, Ann. Ch. Pharm. cxvii. 334: cxvii. 1.)—This acid is a product of the action of nitrous acid on oxybenzamic acid:

$$2C^7H^7NO^3 \quad + \quad NHO^2 \quad = \quad C^{14}H^{11}NO^4 \quad + \quad 2H^2O.$$

It may be regarded either as a double or conjugated acid composed of a molecule of oxybenzamic acid associated with a molecule of benzoic acid having 2 atoms of hydrogen replaced by 2 atoms of monatomic nitrogen, as represented by the preceding formula, or as a double molecule of oxybenzamic acid having 3 atoms of hydrogen replaced by 1 atom of triatomic nitrogen, in which case it may be called azo-dioxybenzamic acid, and represented by the formula $C^{14}(H^{11}N''')N^2O^4$. The former is the view adopted by Griess for this acid and its homologues.

It is prepared by passing nitrous acid vapour into an alcoholic solution of oxybenzamic acid externally cooled (the aqueous solution does not yield a pure product), or better by mixing nitrite of ethyl (obtained by saturating alcohol in the cold with nitrous acid) with alcoholic oxybenzamic acid, and heating the mixture to about 30°. The acid then separates in microscopic crystals, which may be purified by washing with alcohol.

Diazobenzo-oxybenzamic acid forms crystalline granules or small needles of a fine orange-yellow colour. It has neither taste nor smell, and is nearly insoluble in *water*, *alcohol*, *ether*, *sulphide of carbon*, and *chloroform*. It dissolves in *mineral acids*, especially with aid of heat, but does not separate therefrom without alteration. It dissolves in *potash* and in *ammonia*, and is precipitated from the solution by acids, even by acetic acid. It may be dried at 100° without decomposition, but at 180° it explodes and gives off gas with violence. *Hydrochloric acid* at a gentle heat, converts it into chlorobenzoic acid and hydrochlorate of oxybenzamic acid, with evolution of nitrogen:

$$C^7H^4N^2O^2.C^7H^7NO^2 \quad + \quad 2HCl \quad = \quad C^7H^5ClO^2 \quad + \quad C^7H^7NO^2.HCl \quad + \quad N^2.$$

*Hydriodic acid* acts in a similar manner, producing iodobenzoic acid $C^7H^5IO^2$, and hydriodate of oxybenzamic acid. A similar action appears also to be exerted by *hydrofluoric acid*, *hydrocyanic acid*, and the *bromide*, *iodide*, &c., of *ethyl*. *Bromine* in the anhydrous state acts with great violence on diazobenzo-oxybenzamic acid, nitrogen and hydrobromic acid being given off, and a resinous mixture formed, consisting of several brominated acids. If bromine be added to the acid suspended in water, the action takes place more quietly, and a product is obtained from which bromobenzoic acid, $C^7H^5BrO^2$, and tribromobenzoic acid, $C^7H^3Br^3O^2$ (or compounds isomeric therewith), may be separated. Brominated derivatives of oxybenzoic acid and of oxybenzamic acid are probably formed at the same time. *Chlorine* acts like bromine. *Iodine* acts less energetically, the dry vapours not attacking the acid at all; but when iodine is added to boiling water in which the acid is suspended, iodoxybenzoic acid is formed, together with hydriodate of oxybenzamic acid. The former of these products is nearly insoluble in water, the latter easily soluble:

$$C^{14}H^{11}N^3O^4 \quad + \quad I^2 \quad + \quad H^2O \quad = \quad C^7H^5IO^3 \quad + \quad C^7H^7NO^2.HI \quad + \quad N^2.$$

*Fuming nitric acid* decomposes diazobenzo-oxybenzamic acid with violence, and sets it on fire. Ordinary concentrated *nitric acid* dissolves it at a gentle heat, forming a reddish liquid, which decomposes at a higher temperature, with violent evolution of red vapours; and the remaining liquid, when evaporated, yields among other products, crystals of trinitroxybenzoic acid, $C^7H^3(NO^2)^3O^3$. *Nitrous acid* passed into boiling water in which diazobenzo-oxybenzamic acid is suspended, converts it into nitroxybenzoic acid, $C^7H^5(NO^2)O^3$, with evolution of nitrogen. Probably oxybenzoic acid is first formed, according to the equation:

$$C^{14}H^{11}N^3O^4 \quad + \quad NHO^2 \quad = \quad 2C^7H^6O^3 \quad + \quad N^4.$$

But if the diazobenzo-oxybenzamic acid be suspended in *alcohol* previously saturated with nitrous acid, an additional quantity of nitrous gas then passed into it, and the alcohol afterwards evaporated, a red-brown residue is obtained, consisting chiefly of salylic acid. The reaction appears to take place as follows:

$$\underset{\text{Diazobenzo-oxybenzamic acid.}}{C^{14}H^{11}N^3O^4} + \underset{\text{Alcohol.}}{2C^2H^6O} + \underset{\text{Nitrous acid.}}{NHO^2} = \underset{\text{Salylic acid.}}{2C^7H^6O^2} + \underset{\text{Aldehyde.}}{2C^2H^4O} + 2H^2O + N^4.$$

When a solution of diazobenzo-oxybenzamic acid in aqueous ammonia is evaporated till nitrogen ceases to escape, then a little further concentrated on the water-bath, and mixed with hydrochloric acid, a red amorphous substance separates, having apparently the composition $C^{14}H^{10}O^5$; and the liquid retains oxybenzamic acid combined with hydrochloric acid:

$$2C^{14}H^{11}N^3O^4 \quad + \quad H^2O \quad = \quad C^{14}H^{10}O^5 \quad + \quad 2C^7H^7NO^3 \quad + \quad N^4.$$

**Diazobenzo-oxybenzamates.** The acid dissolves in alkalis, neutralising them completely, and expels carbonic acid from carbonates. The general formula of its salts is $C^{14}H^9M^2N^3O^4$, or $C^{14}H^9M''N^3O^4$, according to the atomicity of the metal. The diazobenzo-oxybenzamates of the alkali-metals are easily soluble in water, stable when dry, but decompose easily in solution, giving off nitrogen gas. With solutions of the earth-metals and heavy metals, the acid forms insoluble or sparingly soluble precipitates.

The *ammonium-salt*, $C^7H^9(NH^4)^2N^3O^4$, forms microscopic needles. The *potassium-salt*, $C^7H^9K^2N^3O^4$, is best prepared by dissolving the acid in a large excess of carbonate of potassium heated to about 80°. It then separates on cooling in extremely small yellowish-white needles, which exhibit brilliant iridescence while floating in the mother-liquor. It dissolves readily in hot water, crystallising therefrom in nodules; sparingly in a strong solution of carbonate of potassium; not at all in alcohol or ether. After drying in the air, it does not give off any thing at 160°, but detonates at a higher temperature. The *sodium-salt* closely resembles the potassium-salt. The *barium-salt*, $C^{14}H^9Ba''N^3O^4$, is obtained by mixing the solution of the potassium-salt with nitrate of barium, as a yellowish-white crystalline precipitate, nearly insoluble in water, quite insoluble in alcohol and ether. The *calcium-salt* is very similar. The *magnesium-salt* crystallises in yellow needles often grouped in small spheres, readily soluble in water. The *ferric salt* is a yellow precipitate. The *zinc-salt* is yellowish, amorphous, insoluble in water. The *copper-salt* when dry is a greenish amorphous powder. The *mercuric salt* is a yellow-green precipitate. The *silver-salt*, $C^{14}H^9Ag^2N^3O^4$, obtained by treating a neutral solution of the ammonium-salt with nitrate of silver, is a greenish-yellow gelatinous precipitate, yellow when dry, insoluble in water, alcohol, and ether, permanent at 100° C, detonating at higher temperatures.

*Diazobenzo-oxybenzamic ethers.* The *ethylic* compound, $C^{14}H^9(C^2H^5)^2N^3O^4$, is obtained by passing nitrous acid gas into an alcoholic solution of ethylic oxybenzamate, and separates in yellow crystals, which quickly increase, and cause the liquid to solidify, if not too dilute. By washing with cold alcohol, and recrystallisation from boiling alcohol, the ether is obtained in golden-yellow capillary needles. It is insoluble in water, moderately soluble in boiling alcohol and ether. Melts at 144°, but does not solidify again till it has been kept for a day at a low temperature. When strongly heated, it decomposes with evolution of nitrogen. It dissolves, though with difficulty, in dilute acids, and is precipitated by ammonia.

The *methylic ether*, $C^{14}H^{8}(CH^{3})^{2}N^{2}O^{4}$, may be prepared like the ethyl-compound, or better by passing nitrous acid into an ethereal solution of methylic oxybenzamate. It separates in crystalline spherules, which dissolve with moderate facility in warm alcohol, and separate on cooling either in the same form or in obtuse lancet-shaped yellow crystals. It is insoluble in water, melts at 160°, and exhibits the same peculiarity in solidifying as the ethyl-compound, which it likewise resembles in other respects. (Griess.)

**Diazobenzoic Acid.** $C^{7}H^{4}N^{2}O^{2} = \left.\begin{matrix}C^{7}H^{3}N^{2}O\\H\end{matrix}\right\}O$. (Griess, Ann. Ch. Pharm. cxx. 125).—This acid is separated by alkalis from its compound with nitric acid, as a yellow mass which quickly decomposes. It unites with other acids, namely with nitric and hydrochloric acids, and with oxybenzamic acid, forming the acid just described.

*Nitrato-diazobenzoic acid*, $C^{7}H^{5}N^{3}O^{5} = C^{7}H^{4}N^{2}O^{2}.NHO^{3}$, is produced by the action of nitrous acid on a cold solution of oxybenzamic acid in aqueous or alcoholic nitric acid. It separates from the solution in white prisms, which dissolve sparingly in cold water, and explode violently when heated. Boiling water decomposes it quickly, with evolution of nitrogen, separation of nitric acid, and probably with formation of oxybenzoic acid: perhaps thus,

$$C^{7}H^{4}N^{2}O^{2}.NHO^{3} \quad + \quad H^{2}O \quad = \quad C^{7}H^{6}O^{3} \quad + \quad N^{2} \quad + \quad NHO^{3}.$$

*Ethylic nitrato-diazobenzoate* is obtained by the action of nitrous acid on ethylic nitrato-oxybenzamate; its aqueous solution mixed with *auric chloride* yields a gold-salt, $C^{7}H^{3}(C^{2}H^{5})N^{2}O^{2}.HCl.AuCl^{3}$, which crystallises from alcohol in golden-yellow prisms.

The *platinum-salt of chlorhydrato-diazobenzoic acid*, $2C^{7}H^{4}N^{2}O^{2}.2HCl.Pt^{iv}Cl^{4}$, is obtained in yellow prisms on mixing an aqueous solution of nitrato-diazobenzoic acid with platinic chloride. When treated with sulphydric acid, it yields sulphoxybenzoic acid, probably thus,

$$2C^{7}H^{4}N^{2}O^{2}.2HCl.PtCl^{4} \quad + \quad 4H^{2}S \quad = \quad 2C^{7}H^{6}O^{2}S \quad + \quad 6HCl \quad + \quad PtS^{2}.$$

**Dioxybenzamic Acid.** $C^{7}H^{8}N^{2}O^{2} = \left.\begin{matrix}H^{4}\\(C^{7}H^{3}O)'''\\H\end{matrix}\right\}\begin{matrix}N^{2}\\O\end{matrix}$. (Voit, Ann. Ch. Pharm. xcix. 106.)—This acid, which may be regarded as a diamic acid derived from a hypothetical dioxybenzoic acid, $\left.\begin{matrix}(C^{7}H^{3}O)'''\\H^{3}\end{matrix}\right\}O^{3}$, or else as diamido-benzoic acid, $C^{7}H^{4}(NH^{2})^{2}O^{2}$, is formed by the reduction of dinitrobenzoic acid by sulphuretted hydrogen or ferrous acetate. A hot ammoniacal solution of dinitrobenzoic acid is saturated with sulphuretted hydrogen, filtered, evaporated on the water-bath, saturated with hydrochloric acid, and filtered hot; and the crystals of hydrochlorate which separate are converted into sulphate, and decomposed by barytic carbonate. The filtrate on evaporation (first over a water-bath, finally over sulphuric acid), yields small, greenish, pointed crystals of dioxybenzamic acid, which have no taste, are neutral to litmus, and soluble in water, alcohol, or ether; they melt and blacken at 195°, and cannot be sublimed. Nitrous fumes passed into its hot solution from a red resinous mass.

This compound is no acid, for it does not combine with bases; on the contrary, it combines with several acids, forming definite, mostly crystallisable salts. The *acetate*, obtained by decomposing the sulphate with acetate of barium, turns brown on evaporation, and finally deposits brownish prismatic crystals. The impure *hydrochlorate* obtained as above, is purified by solution in water and addition of hydrochloric acid; the pure compound, $C^{7}H^{8}N^{2}O^{2}.2HCl$, is then obtained in white needles, soluble in water, alcohol, or ether. Its solution decomposes in the air, or when heated. It does not precipitate platinic chloride, but the mixture, when evaporated over sulphuric acid, yields brown crusts of the *chloroplatinate*, $2C^{7}H^{8}N^{2}O^{2}.4HCl.Pt^{iv}Cl^{4}$. The *nitrate* and *oxalate* are both crystalline and dark-coloured; the *sulphate* may be obtained almost colourless by recrystallisation from alcohol; it is less soluble in alcohol than in water. F. T. C.

**OXYBENZODIAMIDE.** $C^{7}H^{8}N^{2}O = \left.\begin{matrix}(C^{7}H^{4}O)''\\H^{4}\end{matrix}\right\}N^{2}$, or *Amidobenzamide*, $\left.\begin{matrix}C^{7}H^{4}(NH^{2})O\\H^{2}\end{matrix}\right\}N$. (Chancel, Ann. Ch. Pharm. lxii. 274.)—This compound, isomeric with phenyl-carbamide or aniline-urea (i. 755), is obtained by the action of sulphide of ammonium on nitrobenzamide in aqueous solution:

$$\left.\begin{matrix}C^{7}H^{4}(NO^{2})O\\H^{2}\end{matrix}\right\}N \quad + \quad 3H^{2}S \quad = \quad \left.\begin{matrix}(C^{7}H^{4}O)''\\H^{4}\end{matrix}\right\}N^{2} \quad + \quad 2H^{2}O \quad + \quad S^{3}.$$

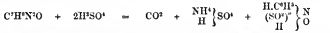
It separates from the solution in crystals containing 1 at. water ($C^{7}H^{8}N^{2}O.H^{2}O$), which it gives off at 100°—120°. It is soluble in *water*, *alcohol*, and *ether*, but the alcoholic solution quickly turns red and appears to decompose. Crystallised oxybenzodiamide melts at 72°; the dehydrated compound above 100°; at higher temperatures it decomposes, leaving a carbonaceous residue. When gently heated with *potash-lime*, it is resolved into ammonia and oxybenzamate of potassium:

$$C^7H^8N^2O \quad + \quad KHO \quad = \quad NH^3 \quad + \quad C^7H^6KNO^3,$$

the latter being further resolved, at a higher temperature, into aniline and potassic carbonate:

$$C^7H^6KNO^3 \quad + \quad KHO \quad = \quad C^6H^7N \quad + \quad K^2CO^3.$$

Heated with *sulphuric acid*, it is resolved into carbonic anhydride, acid sulphate of ammonium, and phenyl-sulphamic acid:



$$C^7H^8N^2O \quad + \quad 2H^2SO^4 \quad = \quad CO^2 \quad + \quad \left.\begin{matrix}NH^4\\H\end{matrix}\right\}SO^4 \quad + \quad \left.\begin{matrix}H.C^6H^5\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$$

Oxybenzodiamide unites with acids. The *nitrate*, $C^7H^8N^2O.NHO^3$, forms crystalline crusts or nodular groups of prisms sparingly soluble in water. On mixing moderately dilute solutions of oxybenzodiamide and silver-nitrate at the boiling heat, the liquid on cooling deposits the compound $C^7H^8N^2O.NAgO^3$ in needles which become coloured when exposed to light. The *hydrochlorate*, $C^7H^8N^2O.HCl$, crystallises from aqueous solution in small needles. A solution of oxybenzodiamide in boiling water, mixed with excess of hydrochloric acid, and then with platinic chloride, yields long orange-coloured prisms of the *platinum-salt*, $2C^7H^8N^2O.H^2Cl^2.Pt^{iv}Cl^4$. (Chancel.)

An ethereal solution of oxybenzodiamide treated with *nitrous acid*, yields white explosive needles of nitrate of diazobenzamide, $\left.\begin{matrix}C^7H^3N^2O\\H^2\end{matrix}\right\}N.NHO^3$, which, when treated with hydrochloric acid and platinic chloride, yields the salt $2C^7H^8N^2O.H^2Cl^2.Pt^{iv}Cl^4$. (Griess, Ann. Ch. Pharm. cxx. 127.)

**OXYBENZOIC ACID.** $C^7H^6O^3 = \left.\begin{matrix}H\\(C^7H^4O)''\\H\end{matrix}\right\}O^2$. (Gerland, Ann. Ch. Pharm. xci. 185.—Griess, *ibid.* cxvii. 1; Zeitschr. Ch. Pharm. 1862, p. 97.)—An acid metameric with salicylic acid, obtained: 1. By the prolonged action of nitrous acid on oxybenzamic acid (Gerland). In this reaction, which yields but a small quantity of oxybenzoic acid, diazobenzo-oxybenzamic acid is first formed, and afterwards partially converted into oxybenzoic acid (Griess, p. 292).—2. It is much more easily obtained by decomposing nitrato-diazobenzoic acid with boiling water (Griess):

$$C^7H^4N^2O^2.NHO^3 \quad + \quad H^2O \quad = \quad C^7H^6O^3 \quad + \quad NHO^3 \quad + \quad N^2.$$

Oxybenzoic is a colourless or yellowish crystalline powder, sparingly soluble in cold *water* and *alcohol*, easily soluble in the same liquids at boiling heat; the solutions are strongly acid. It melts at a high temperature, and distils without decomposition; volatilises with vapour of water when its aqueous solution is boiled, and condenses in shining needles. It is permanent in the air, and does not lose weight at 100°. When quickly heated, it splits up (like salicylic acid) into carbonic anhydride and phenylic alcohol; the decomposition takes place more easily when the acid is heated with slaked lime. It is distinguished from salicylic acid by the fact that its aqueous solution is not coloured violet by ferric salts. (Gerland.)

Oxybenzoic acid is monobasic; it displaces carbonic acid and neutralises alkalis. The oxybenzoates of the alkali-metals are very soluble and difficult to crystallise; those of the alkaline earth-metals are less soluble and crystallise in needles; the rest are insoluble in water and in alcohol, but soluble in acids. The *lead-salt* contains $C^{14}H^{10}Pb''O^6$. (Gerland.)

*Iodoxybenzoic acid*, $C^7H^5IO^3$.—Produced by the action of iodine on diazobenzo-oxybenzamic acid (p. 292). It usually crystallises in long narrow colourless laminæ, which sublime at a gentle heat, but are decomposed when quickly heated, giving off vapours of iodine. (Griess, *loc. cit.*)

*Nitroxybenzoic acid*, $C^7H^5NO^5 = C^7H^5(NO^2)O^3$, is formed by the action of nitric acid of specific gravity 1·36 at ordinary temperatures on oxybenzoic acid; with stronger nitric acid, more highly nitrated products are obtained which explode violently when heated (Gerland). The mononitrated acid is also produced by the action of nitrous acid on diazobenzo-oxybenzamic acid. (Griess.)

Nitroxybenzoic acid dissolves in hot water, and separates on evaporation in fine yellow crystals belonging to the rhombic system. It has a bitter, disagreeable taste, and imparts a yellow colour to a large quantity of water. It is strongly acid and displaces carbonic acid. Sulphide of ammonium decomposes it, with precipitation of sulphur.

*Nitroxybenzoate of potassium*, $C^7H^4K(NO^2)O^3$, is sparingly soluble in cold, easily soluble in boiling water, and crystallises therefrom in beautiful golden-yellow shining prisms, resembling picrate of potassium. It explodes slightly when heated. (Gerland.)

*Trinitroxybenzoic acid*, $C^7H^3N^3O^9 = C^7H^3(NO^2)^3O^3$, is produced by the action of ordinary nitric acid at a gentle heat on diazobenzo-oxybenzamic acid. It crystallises in nearly white rhombic prisms, which have an intensely bitter taste, dissolve easily in water, alcohol, and ether, forming yellow solutions, melt when heated, and detonate violently at higher temperatures. The acid is decomposed by sulphide of ammonium, with separation of sulphur, and formation of a new compound.

The trinitroxybenzoates, $C^7HM^2N^3O^9$ or $C^7HM''N^3O^9$, are nearly all soluble in water, and some of them form fine crystals. The *ammonium-salt* contains $C^7H(NH^4)^2N^3O^9.2H^2O$; the *barium-salt* and the *silver-salt* are anhydrous. (Griess.)

**OXYBUTYRIC ACID.** This name is sometimes applied to Wurtz's butylactic acid, $C^4H^8O^3$ (i. 688), produced by the action of dilute nitric acid on hydrate of amylene. Friedel and Machuca, however (Ann. Ch. Pharm. cxx. 279), apply it to an acid having the same composition as butylactic acid, but differing from it in some respects, which is obtained by oxidising dibromobutyric acid with silver-oxide. It forms a *zinc-salt* containing $C^8H^{14}Zn''O^6$, which crystallises in radiate nodules, not in nacreous laminæ, like the butylactate. The acid separated from the zinc-salt yields on evaporation a syrup which crystallises in vacuo or over oil of vitriol, in deliquescent rosettes.

**OXYBUTYROXYL-PROPIONIC ETHER.** Kolbe's name for Wurtz's butyrolactic ether, $\left.\begin{matrix}C^4H^7O\\(C^3H^4O)''\\C^2H^5\end{matrix}\right\}O^2$, which he represents by the formula*

$$C^4H^5O,\ C^4\left\{\begin{matrix}H^4\\C^6\left\{\begin{matrix}H^6\\HO^2\end{matrix}\right\}C^2O^2\end{matrix}\right\}[C^2O^2],O.$$

**OXYCARBOXYLIC ACID.** $C^{10}H^{20}O^{22}$.—An acid produced by the action of chlorine or nitric acid on trihydrocarboxylic acid (iii. 189). It crystallises in hard, colourless, rhombic prisms, insoluble in alcohol or ether, sparingly soluble in cold water, easily soluble in dilute nitric acid. When heated to 100°, or treated with warm water or with bases, it becomes brown-red, and is converted, with evolution of gas, into dihydrocarboxylic acid. (Lerch, Ann. Ch. Pharm. cxxiv. 20.)

*Carboxylic acid*, $C^{10}H^4O^{10}$, is known only in its salts, which are formed by oxidation of the hydrogen in the trihydro-, dihydro-, and hydro-carboxylates. The *neutral potassium-salt*, $C^{10}K^4O^{10}$, is black, but turns red when exposed to the air. A green crystalline *potassium-salt*, $C^{10}HK^3O^{10}$, the corresponding *ammonium-salt*, $C^{10}H(NH^4)^3O^{10}$, and a red acid *potassium-salt*, $C^{10}H^2K^2O^{10}$, have likewise been obtained. These salts when decomposed by acids, yield, not carboxylic but rhodizonic acid, according to the equation:

$$\underset{\text{Carboxylic acid.}}{C^{10}H^4O^{10}} + 2H^2O = \underset{\text{Rhodizonic acid.}}{2C^5H^4O^6}.$$

**OXYCARMINIC ACID.** $C^9H^8O^7$.—An acid, said by Schützenberger (Ann. Ch. Phys. [3] liv. 52) to exist in cochineal, together with carminic acid (see CARMINE, i. 804).

**OXYCHLORIC ACID.** Syn. with PERCHLORIC ACID (see CHLORINE, OXIDES AND OXYGEN-ACIDS OF, i. 910).

**OXYCHLORIDES.** Also called *Basic Chlorides.* Compounds of metallic chlorides with the basic oxides of the same metals; they may be formulated on the type $\left.\begin{matrix}mH^2Cl\\nH^2O\end{matrix}\right\}$. They are produced by imperfect precipitation of a metallic chloride with an alkali, *e. g.* of mercuric chloride by lime-water; by the action of water on metallic chlorides, as in the precipitation of antimonious chloride by water; by the partial decomposition of chlorides by oxygen, or of oxides by chlorine at high temperatures. Several oxychlorides occur as natural minerals, having been formed by the action of air and water on chlorides (see the several METALS).

**OXYCHLOROCARBONIC ACID.** Syn. with CHLORIDE OF CARBONYL OF PHOSGENE (i. 774).

**OXYCINCHONINE.** $C^{20}H^{24}N^2O^2$. (H. Strecker, Ann. Ch. Pharm. cxxiii. 379.)—A base isomeric with quinine, obtained by the action of potash or silver-oxide on an alcoholic solution of dibromocinchonine (i. 978). By passing carbonic acid gas into the solution after prolonged boiling till the potash is neutralised, then evaporating, treating the residue first with water, then with alcohol, and leaving the alcoholic solution to cool, oxycinchonine is obtained in colourless crystalline laminæ, easily soluble in acids. The solutions are not fluorescent, and do not become green on addition of chlorine-water and ammonia. The *neutral sulphate*, $2C^{20}H^{24}N^2O^2.H^2SO^4$, crystallises well. The *chloroplatinate*, $C^{20}H^{24}N^2O^2.H^2Cl^2.Pt^{iv}Cl^4$, is light yellow, sparingly soluble in hot water, insoluble in alcohol and ether. The di-acid salts do not crystallise.

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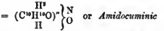
* H = 1, C = 6, O = 8.

**OXYCOBALTIC SALTS.** See Cobalt-bases, Ammoniacal (i. 1056).

**OXYCROCONIC ACID.** Syn. with Leuconic Acid (iii. 584).



**OXYCUMINAMIC ACID.** $C^{10}H^{13}NO^3 = \left.\begin{array}{c} H^2 \\ (C^{10}H^{10}O)'' \\ H \end{array}\right\} \begin{array}{c} N \\ O \end{array}$ or *Amidocuminic acid*, $C^{10}H^{11}(NH^2)O^2$.—An acid derived from oxycuminic acid in the same manner as its homologue oxybenzamic acid is derived from oxybenzoic acid (see Cuminic Acid, ii. 179).

*Diazocumin-oxycuminamic acid*, $C^{20}H^{23}N^3O^4 = C^{10}H^{10}N^2O^2.C^{10}H^{13}NO^2$, is obtained by the action of nitrous acid on an alcoholic solution of oxycuminamic acid cooled with ice, carefully avoiding an excess of nitrous acid. It crystallises in yellow microscopic prisms or laminæ. It is the least stable of all the compounds of the series, being decomposed with evolution of nitrogen when boiled with alcohol. Its reactions are precisely analogous to those of diazobenzo-oxybenzamic acid (p. 291).

**OXYCUMINIC ACID.** $C^{10}H^{12}O^3$. See Cuminic Acid (ii. 179).

**OXYDIBROMOPHENYL-SULPHURIC ACID.** $C^6H^4Br^2SO^4$.—An acid produced by the action of boiling water on diazo-dibromophenyl-sulphuric acid (see Phenyl-sulphuric Acid).

**OXYFLUORIDES.** Compounds analogous to the oxychlorides, and referrible to the type $\left.\begin{array}{r} mHF \\ nH^2O \end{array}\right\}$.

**OXYGEN.** Atomic weight 16. Symbol O.—Synonymes: *Oxygène*, *Oxygenium*, *Sauerstoff*, *Vital Air*, *Pure Air*, *Dephlogistigated Air*, *Feuerluft*, *Acidifying principle*.

Oxygen is the most abundant of all the elements. It forms eight-ninths of water, nearly one-fourth of the air, and about one-half of silica, chalk, and alumina, the three most plentiful constituents of the earth's surface. With a few exceptions only, of which the principal are rock-salt, fluor-spar, blende, galena, and pyrites, it enters into the constitution of all important rocks and minerals. Independently of its existence in the water of the tissues, it is an essential constituent of all living organisms. It is absorbed by animals during respiration, and evolved in the free state by growing vegetables when exposed to sunlight. The oxygen of the atmosphere is mechanically mixed with the nitrogen and other constituents, but is chemically free or uncombined. Oxygen gas was discovered by Priestley in 1774, and a year later by Scheele (see Gas, ii. 773). Its name is derived from ὀξύ, acid, and γεννᾶν, to produce, because it was formerly regarded as essential to the constitution of an acid. (See Acids, i. 41.)

*Preparation.*—1. Oxygen gas may be prepared by applying a greater or less degree of heat to various oxidised substances, such, for instance, as the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, barium, lead and manganese; and the chlorates, nitrates, bichromates, &c., of potassium and other bases.

α. *Oxide of mercury* is interesting as being the substance from which oxygen was originally obtained. By heating it in a flask, it breaks up into mercury-vapour, which may be condensed in a receiver, and oxygen gas, which may be collected over water.

β. *Peroxide of manganese* is a very cheap source of oxygen when large quantities are required. The substance should be heated to redness in an iron bottle, whereby oxygen gas is given off, and a lower oxide of manganese left behind: $3MnO^2 = Mn^3O^4 + O^2$.

γ. *Chlorate of potassium*, however, constitutes the most generally available source of the gas for preparation on the laboratory scale. When strongly heated in a flask of hard glass, it melts, gives off the whole of its oxygen, and leaves a residue of chloride of potassium: $KClO^3 = KCl + O^3$. The temperature required to effect this decomposition completely is so high, that the flask, though made of difficultly fusible glass, usually becomes softened, and yields to the pressure of the gas, which at last forces an opening through its side or bottom. It is found that the chlorate gives off its oxygen at a much lower temperature when mixed with about one-eighth of its weight of some metallic oxide, such as that of copper, or iron, or manganese. Under these circumstances, the salt does not fuse; but the resulting gas is less pure than when the unmixed chlorate is employed.

δ. A concentrated aqueous solution of *hypochlorite of calcium* (bleaching powder), gently heated with a small quantity of peroxide of cobalt, is completely resolved into chloride of calcium and oxygen. The gas is evolved with great ease and regularity, so that the method is well adapted for the preparation of large quantities. The same quantity of cobalt-peroxide (about $\frac{1}{2}$ to $\frac{1}{10}$ of the weight of the bleaching powder) may be repeatedly used for the purpose, as it does not undergo any permanent change, but appears to act merely as a carrier of oxygen, first taking it from the hypochlorite and passing to a higher state of oxidation, and then giving it up again. The special preparation of the cobalt-peroxide may even be dispensed with altogether, a few drops of any cobalt-solution being simply added to the solution of bleaching powder at the commencement of the process; the cobalt is then immediately converted into peroxide by the oxidising action of the hypochlorite. It is necessary to use a clear solution of bleaching powder, as if milky it is apt to froth considerably. (**Fleitmann**, Ann. Ch. Pharm. cxxxiv. 64.)

ε. *Peroxide of barium*, when strongly heated, gives up one-half its oxygen to produce baryta: $BaO^2 = BaO + O$. By passing a current of moist air over the less heated baryta, it absorbs oxygen and re-produces the peroxide, which a stronger heat again decomposes; so that, by repetitions of the process, a small quantity of the peroxide can, as was shown by **Boussingault** (Chem. Soc. Qu. J. v. 269), furnish an indefinitely large quantity of oxygen. A patent for the preparation of oxygen in this manner and its application in various chemical operations, has been taken out by Messrs. Swindells and Nicholson (Chem. Gaz. 1855, p. 139).

ζ. **Deville** and **Debray** (Compt. rend. li. 822; Ann. Ch. Pharm. cxvii. 295) recommend for the preparation of oxygen on the large scale:—1. The ignition of zinc-sulphate, which at a temperature not higher than that required for the decomposition of peroxide of manganese, gives off a mixture of sulphurous acid and oxygen.—2. The decomposition of sulphuric acid, which, when passed in the state of vapour over red-hot platinum-foil or platinum sponge, is resolved into sulphurous acid and oxygen. By passing the gaseous mixture obtained by either of these processes through water or an alkaline solution, the sulphurous acid is absorbed, and the oxygen set free. The aqueous sulphurous acid thus obtained may be utilised in the manufacture of sulphuric acid. The decomposition of sulphuric acid in this way is recommended by **Deville** and **Debray**, also by **De Luca** (Compt. rend. liii. 156), as the cheapest of all methods of obtaining oxygen in large quantities.

η. Another method which has been proposed for obtaining oxygen on the manufacturing scale is the ignition of a mixture of nitrate of sodium and oxide of zinc. (See an examination of this process by **J. H. Pepper**, Chem. News, vi. 218.)

2. Oxygen may also be prepared by the action of sulphuric acid, at a moderate temperature, upon certain highly oxidised compounds, such as the peroxides of lead and manganese, the bichromate and permanganate of potassium, &c. These reactions are seldom employed for the purpose of obtaining free oxygen gas, but are extremely convenient as means for affording oxygen to various other bodies, or, in other words, for oxidising them. Thus hydrochloric acid HCl, when treated with sulphuric acid and permanganate of potassium, becomes hypochlorous acid HClO. Alcohol $C^2H^6O$, when treated with sulphuric acid and peroxide of manganese, yields aldehyde $C^2H^4O$, and water $H^2O$. Cuminic acid $C^{10}H^{12}O^2$, treated with sulphuric acid and acid chromate of potassium, yields insolinic acid $C^9H^8O$, together with carbonic anhydride $CO^2$ and two atoms of water $2H^2O$. The reactions, so far as regards the evolution of oxygen, are as follows:

$$H^2SO^4 + MnO^2 = MnSO^4 + H^2O + O$$

$$2H^2SO^4 + KMnO^4 = K\overset{'''}{Mn}(SO^4)^3 + 2H^2O + O^2$$

$$4H^2SO^4 + K^2Cr^2O^7 = 2\{K\overset{'''}{Cr}(SO^4)^2\} + 4H^2O + O^3$$

3. Oxygen may be obtained by the electrolysis of water, being liberated at the positive pole. (See ELECTRICITY, ii. 432.)

4. When fresh mint, or parsley, or other active leafy plant, is immersed in carbonic acid water and exposed to sunlight, oxygen is liberated from the leaves in considerable quantities. The experiment is best conducted in a tall inverted cylinder, so that the oxygen gas may collect in its upper part, by displacement of the carbonic acid water which should originally fill the vessel.

5. There are numerous other reactions which serve to liberate oxygen, but they are not employed as means for the preparation of the gas. Some of them, however, are very interesting. Thus when oxide of silver reacts with peroxide of hydrogen, there are produced water, metallic silver, and oxygen:

$$H^2O^2 + Ag^2O = H^2O + Ag^2 + O^2.$$

*Properties.*—Oxygen is colourless, tasteless, and inodorous. It is the least refractive of all the gases. It has resisted every attempt to effect its liquefaction. It is the most magnetic of all gases (see MAGNETISM, iii. 773). It is heavier than atmospheric air in the proportion of 1·1056 to 1·0000. It is very sparingly soluble in water, 100 volumes of which at ordinary temperatures can only retain about 3 volumes of the gas. (See Gases, Absorption of, ii. 797.) Nearly all natural waters contain dissolved oxygen, and can only be freed therefrom by prolonged ebullition in vacuo. The chemical reactions of atmospheric air depend principally upon the oxygen which it contains; the air being, in its chemical relations, merely oxygen gas mixed, or diluted, with about four times its volume of nitrogen.

Oxygen in the free state, whether or not diluted with nitrogen, manifests considerable chemical activity, even at ordinary temperatures. With the single exception of fluorine, it has been made, directly or indirectly, to unite with every known element. Some reactions of oxygen are interesting from their employment as means for detecting the presence of the gas, or effecting its removal. Thus an alkaline solution of *white indigo* absorbs oxygen rapidly, at the same time becoming blue. An alkaline solution of a *pyrogallate* absorbs oxygen, forming an opaque black liquid. *Nitric oxide gas*, which is perfectly colourless, unites with oxygen to form deep orange-red vapours. *Phosphorus* slowly absorbs oxygen, as do also moist *iron-wire*, moist *lead-turnings*, moist *saw-dust*, and many metallic compounds, such, for instance, as ammonio-subchloride of copper, or chloride of cuprosammonium, the protohydrates of iron and manganese, the white double cyanide of potassium and iron, &c.

The majority of the metals, when in the massive state, remain perfectly bright and unacted upon in dry oxygen or air; but in moist oxygen or air, many of them become slowly oxidised. The coating of oxide first formed frequently protects the metal from more than a superficial oxidation, as is notably the case with lead. Some of the ordinarily permanent metals, when in a very finely divided state, for instance lead as obtained by the ignition of its tartrate, and iron as produced by the ignition of Prussian blue, undergo so violent an oxidation, that spontaneous combustion results from their mere exposure to air or oxygen. Hence they are termed *pyrophori*. Various other bodies, which expose a large surface to the action of air or oxygen, become gradually heated through slow oxidation, and finally undergo spontaneous combustion. Greasy tow and woollen refuse are peculiarly liable to this action.

Many substances, when heated to redness, unite with oxygen, and thereby give rise to the phenomena of combustion or burning. The combustions of phosphorus, charcoal, sulphur, iron, zinc, and naphthalene, in undiluted oxygen, constitute very brilliant experiments. In each case the results are oxidised compounds of the substance burned. The weight of oxidised products corresponds exactly with the weight of the body burned, plus the weight of the oxygen consumed. When an ordinary combustible body, such as wood, paper, or wax candle, is inflamed in air and then immersed in a vessel of oxygen, the combustion proceeds with greatly increased intensity. If the flame of the wood, paper, or wax candle be extinguished, and any portion of the substance be left in a glowing state, it will, when immersed in oxygen, immediately burst into flame. This is a very characteristic property of undiluted, or but slightly diluted, oxygen, which it shares only with nitrous oxide gas. A jet of hydrogen gas burns in oxygen as in air, but more rapidly. Of course the two gases can only unite where they are in contact with one another, that is immediately around the jet of hydrogen. Hence formerly the hydrogen was said to burn, and the oxygen merely to support combustion. But if a jet of oxygen be introduced into a vessel of hydrogen, the flame will proceed from the oxygen and the hydrogen become the supporter of combustion. For this purpose the hydrogen, contained in a somewhat narrow-mouthed inverted jar, should be ignited at the mouth of the jar. Then the jet of oxygen, in passing through the flame, will itself become ignited and burn in the interior of the jar. In like manner, oxygen may be made to burn in ammonia-gas, by introducing it through a bent tube into a wide-mouthed flask in which strong aqueous ammonia is kept in a state of gentle ebullition, and applying a lighted taper to the end of the tube. (Heintz, Ann. Ch. Pharm. cxxx. 102.)

Respecting the evolution of light and heat in oxidation, the conditions of inflammability, the nature of flame, &c., see Combustion (i. 1089). Respecting the quantities of heat evolved in the oxidation of various bodies, see Heat (iii. 102).

Oxygen is capable of replacing, directly or indirectly, hydrogen, chlorine, bromine, iodine, &c., one atom of oxygen always taking the place of two atoms of each of those elements; thus in the conversion of alcohol into acetic acid by direct oxidation, and of pentachloride of phosphorus into the oxychloride by the action of water, we have:

$$C^2H^4O^2 \quad = \quad C^2H^6O \quad + \quad O \quad - \quad H^2$$
$$PCl^3O \quad = \quad PCl^5 \quad + \quad O \quad - \quad Cl^2.$$

**Active Oxygen or Ozone**—Under certain circumstances, oxygen gas acquires a greatly increased chemical activity, together with a peculiar smell. In this state it constitutes ozone (ὄζειν), and has the characteristic property of decomposing iodide of potassium, with liberation of iodine. Oxygen gas through which electric sparks have been passed, that in which phosphorus, ether, turpentine, and some other substances have been slowly oxidising, and that produced by the electrolysis of an acid liquid, alike react with iodide of potassium as above described. According to Andrews, the ozone produced by these three processes is the same, and consists solely of oxygen in an allotropic state. According to Williamson and Baumert, the ozone produced by electrolysis is a trioxide of hydrogen $H^2O^3$, as is probably also that produced by the oxidation of phosphorus. With regard to the ozone produced by electrical discharges, they admit that perfectly dry oxygen is capable of being modified by such discharges, but consider that the peculiar properties of ozone are not manifested until the action of moisture upon the modified oxygen has resulted in the formation of trioxide of hydrogen. The recent conjoint experiments of Andrews and Tait, however, and likewise those of v. Babo, seem to have established the correctness of the former view.

More than half a century after Van Marum's original observation, that oxygen through which electric sparks had been passed acquired a peculiar smell and the power of attacking mercury, Schönbein, in 1840 (Pogg. Ann. l. 616), published his first paper on ozone. He showed that in the electrolysis of acidulated water, an odorous gas was produced at the positive pole, which might be preserved for a long time in well closed vessels. He also observed the same product to result from the discharges in air of a common electrical machine, and recognised the identity of the smell with that accompanying a flash of lightning. Soon after he noticed the production of ozone by the slow oxidation of phosphorus in moist air or oxygen. Marignac and De la Rive then showed that ozone might be obtained by passing electric sparks through perfectly dry oxygen, a result confirmed by Frémy and Becquerel (Ann. Ch. Phys. [3] xxxv. 62; Chem. Soc. Qu. J. v. 272), and subsequently by Andrews (Chem. Soc. Qu. J. ix. 168). But they found, on the other hand, that dry air or oxygen did not become ozonised by transmission over dry phosphorus. Frémy and Becquerel ascertained that pure oxygen gas, standing over a solution of iodide of potassium, might be completely absorbed by the passage of electric sparks through it. Dry oxygen, however, as shown by Andrews, can be only partially ozonised by electric discharges, unless, indeed, the ozone be absorbed as fast as it is produced. Houzeau (Chem. Soc. J. viii. 237) noticed the ozonic character of oxygen set free by the action of sulphuric acid upon peroxide of barium. According to De Luca, the oxygen evolved by the action of light upon plants is also ozonic. Schönbein, and also Phipson (Chem. News, viii. 103), have observed that air in contact with the juice of fungi becomes ozonised; the latter also finds that ozone is produced when fresh slices of apple are exposed to the air, and is of opinion that the processes of fermentation, putrefaction, and decay, are likewise attended with ozonisation of the air.

Ozone is best prepared by one or other of the following processes. α. Ozonised air or oxygen may be obtained by placing one or two sticks of clean moist phosphorus in a bottle of air or oxygen, when, after an hour or so, the smell of ozone will be very obvious. The sticks of phosphorus should then be taken out, and the gas washed with water to remove the phosphorous acid. If the phosphorus be allowed to remain in the bottle for several hours, the ozone gradually disappears. Or, a current of moist air may be slowly forced through a succession of large Wolfe's bottles, containing each a few sticks of clean phosphorus, and finally through a U-tube containing water or dilute alkali. The junctions should be as few as possible, and should be effected with sound corks, or preferably by grinding. Ozone may be at once produced by plunging a heated glass rod into a mixture of air and ether-vapour.

β. By electrolysis of water acidulated with sulphuric acid. According to Andrews, a mixture of one volume of sulphuric acid with three volumes of water is most productive; while Baumert recommends the electrolyte to consist of water strongly acidulated with both chromic and sulphuric acids. The following arrangement may be advantageously adopted. A coated wire, having attached to its extremity a piece of crumpled platinum foil, which constitutes the positive electrode, is dipped into the electrolyte contained in a cylindrical porous cell, and an inverted tube-funnel, just sufficiently small to slide into the cell, is suspended therein, over the foil. This funnel serves to collect the oxygen which, during the electrolysis, issues in a continuous stream from its narrow orifice. The negative electrode may be constituted of a plate of platinum foil dipping into another vessel of the electrolyte, surrounding the porous cell. Electrolytic oxygen has not been found to contain more than $\frac{1}{250}$ part of its weight of ozone.

γ. Ozone may be obtained by passing electric discharges through air or oxygen. Oxygen gas, prepared by heating chlorate of potassium, is conducted successively through a strong solution of caustic potash, and over pumice and oil of vitriol. Electrical discharges may then be passed through the gas in its transit, whereby a stream of pure ozonised oxygen is obtained; or the gas may first be collected by displacement in suitable tubes, and then ozonified by the discharge. Andrews usually collects his oxygen in a straight glass tube, one end of which, previously contracted by the blowpipe, is in communication with the supply of gas, while the other end is fused to an almost capillary piece of tubing, bent in the form of a U-gauge. After the tube has been two or three times alternately exhausted by an air-pump, and filled with oxygen, the extremity of the capillary gauge is detached from the air-pump, during the passage of the gas, and dipped into oil of vitriol. The supply of gas is continued for some time longer, and the excess allowed to bubble through the oil of vitriol in its escape. The contracted extremity of the reservoir part of the tube, in communication with the source of oxygen, is then sealed by the blowpipe, and a few bubbles of gas are expelled by gentle warming. Upon cooling, oil of vitriol is drawn into the gauge, so as to confine the oxygen in the reservoir. The free extremity of the gauge is next sealed in such a manner as to leave a small space of air above the oil of vitriol. Then by means of platinum wires, previously fused into the reservoir, electric discharges are passed through the oxygen, whereby it becomes ozonified. In this way, any alteration in the bulk or tension of the oxygen, consequent upon the production or subsequent destruction of the ozone, is recognisable by an alteration in the level of the oil of vitriol in the gauge. Andrews found that the Rühmkorff spark was ill-suited for the production of ozone, and that even the ordinary machine spark was much less effective than the silent discharge, obtained by attaching one of the platinum wires of the reservoir-tube to the prime conductor, and the other to the ground, and turning the machine slowly.

In addition to its property of displacing iodine from iodide of potassium, ozone is found to be rapidly absorbed by mercury, and to be completely destroyed or decomposed at a temperature of 250°—300°. Availing themselves of these properties, Andrews and Tait obtained the following results. When the silent discharge was passed through pure dry oxygen contained in one of the gauge-tubes, condensation was observed to take place, at first rapidly and then more slowly. The maximum contraction ever obtained was equal to $\frac{1}{12}$ of the entire volume of the gas. On heating the contracted or ozonised gas to 300°, it recovered its original volume; and this alternate contraction by the silent discharge, and restoration by a temporary heat, could be repeated an indefinite number of times. The extreme contraction gradually diminished when the tube was set aside for some days. The ordinary electrical spark effected a very small contraction of the gas, not exceeding $\frac{1}{100}$ of the whole; and when the spark discharge was passed through the gas contracted by the silent discharge, an expansion took place corresponding to the excess of contraction effected by the silent discharge, beyond that which the spark-discharge could have produced. By introducing into the reservoirs of the tubes, before filling them with oxygen, small quantities of *mercury* or solution of *iodide of potassium*, contained in thin glass bulbs, and then ozonifying by the silent discharge, so as to produce a much contracted gas, Andrews was able to act upon the ozone with these reagents, which could be set free for the purpose by a smart concussion and consequent fracture of their containing bulbs. After the action of the mercury or iodide of potassium upon the contracted gas, it no longer underwent any permanent expansion when heated to 300°, showing the complete absorption or decomposition of the ozone by the reagent. But very curiously, this absorption of the ozone was not attended with any diminution in the bulk of the contracted oxygen. In other words, the active oxygen absorbed by the reagent occupied no part of the bulk of the ozonised gas, inasmuch as its removal did not diminish that bulk. When the ozone was absorbed by solution of iodide of potassium, the amount of iodine liberated was found to correspond exactly with the amount of original contraction, that is, with the quantity of oxygen which had apparently ceased to occupy space. The above remarkable result seems to be best explained by the following hypothesis. If we consider ozone to be a compound of oxygen with oxygen, and the contraction to be consequent upon their combination, then if one portion of this combined or contracted oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole. Thus, if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one-third of this combined oxygen by mercury, the remaining two-thirds would be set free, and consequently expand to their normal bulk, or two volumes:—

$$\overset{\text{2 vols.}}{\overset{-}{O}\;\overset{+}{O}\;\overset{-}{O}} \quad + \quad \overset{+}{Hg} \quad = \quad \overset{+}{Hg}\;\overset{-}{O} \quad + \quad \overset{\text{2 vols.}}{\overset{+}{O}\;\overset{-}{O}}$$

Upon this hypothesis, Andrews' maximum contraction of $\frac{1}{12}$ would indicate the conversion of $\frac{1}{4}$ of his oxygen into ozone. Similar results have been obtained by v. Babo and Clausius (Ann. Ch. Pharm. Suppl. i. 297; Jahresb. 1863, p. 137).

Andrews also ascertained that a stream of dried electrolytic ozone, when heated to

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decomposition, and passed over phosphoric anhydride, did not afford a trace of moisture. When passed consecutively through solutions of iodide of potassium and oil of vitriol, the increase in the weight of the two liquids, from the absorption of the active oxygen, corresponded exactly with the equivalent of iodine set free, as estimated by Bunsen's volumetric method. But, according to Williamson (Ann. Ch. Pharm. liv. 127) and Baumert (Pogg. Ann. lxxxix. 38; Chem. Soc. Qu. J. vi. 169), dried electrolytic ozone does yield water as a product of its decomposition by heat. According to Baumert, also, dried electrolytic ozone when passed consecutively through solution of iodide of potassium and oil of vitriol, sets free a quantity of iodine corresponding to only $\frac{32}{50}$ of the total increase of weight of the two liquids. Hence the formula, previously suggested by Williamson, $H^2O^3$; for $H^2O^3 = H^2O + O^2$, or $50 = 18 + 32$, whence $O^2 = \frac{32}{50}$ of $H^2O^3$. Andrews' view is however confirmed by the recent experiments of v. Babo (Ann. Ch. Pharm. Suppl. ii. 265; Jahresb. 1863, p. 131), and of Soret (Ann. Ch. Pharm. cxxvii. 38; cxxx. 95). Andrews found that electrolytic ozonised oxygen, when decomposed by heat in one of his gauge-tubes underwent a variable increase of bulk, according to the proportion of ozone present. The expansion, however, never exceeded $\frac{1}{250}$ of the entire volume of gas.

The general characters of ozone are those of an oxidising agent. Thus, it corrodes organic matter, as shown by its rapid action on caoutchouc or vulcanite connectors. It bleaches most vegetable colours, as exemplified particularly by its conversion of indigo into isatin. It oxidates black sulphide of lead into white sulphate of lead, changes the yellow ferrocyanide into the red ferridcyanide of potassium, and colours moist sulphate of manganese brown from formation of the hydrated peroxide. It is absorbed by moist iron, copper, mercury, and silver, with production of their respective oxides. Moist silver is even converted into the state of peroxide. Dry ozone is also readily absorbed by dry mercury and dry iodine.

In some cases, however, ozone acts as a deoxygenant. Thus it decomposes peroxide of hydrogen and peroxide of barium, with evolution of inactive oxygen, derived both from the ozone and the peroxide, as represented hypothetically by the following equation:—

$$\overset{-}{O}\ \overset{+}{O}\ \overset{-}{O} + H^2\,\overset{+}{O}\ \overset{-}{O}\ \overset{+}{O} = 2\ \overset{-}{O}\ \overset{+}{O} + \overset{+}{H^2}\ \overset{-}{O}.$$

Dry ozone is decomposed in unlimited quantity by the dry peroxides of manganese and lead, and by black oxide of copper, these oxides not undergoing any alteration of weight by the reaction. It is also decomposed to an unlimited extent by dry silver leaf or filings. These unlimited effects may be explained by the successive, or simultaneous, occurrence of oxidation and reduction. Thus dry silver leaf is at first obviously oxidised by ozone; and the oxide of silver so formed is then reduced, and so on consecutively.

Ozone is practically insoluble in water and acid solutions. When ozonised gas is passed through potash or soda, the first portions are absorbed, probably from the presence of some organic matter in the alkaline liquid, but after a little time, the ozone passes through apparently unaltered.

Schönbein (Ann. Ch. Pharm. cviii. 157) regards ozone as permanently negative oxygen. He also believes in the existence of a permanently positive oxygen, or *antozone*, which at present is known only in combination; and considers that inactive oxygen is a product of the union of ozone and antozone $\overset{-}{O}\ \overset{+}{O}$.

This idea of the existence of two essentially distinct varieties of oxygen, which is likewise advocated by Meissner (*Untersuchungen über den Sauerstoff*, Hannover 1863. Jahresb. 1863, p. 126), is founded chiefly on certain differences observed in the behaviour of oxygen evolved from the alkaline peroxides on the one hand, and that evolved from peroxide of manganese or peroxide of lead on the other, the former exerting for the most part a reducing, the latter an oxidising action. But Brodie showed several years ago (Phil. Trans. 1850, p. 759), and has further demonstrated by more recent experiments (Phil. Trans. 1863, p. 837; Chem. Soc. J. xvi. 316), that the positive or negative character of oxygen (and indeed of every other element) is not permanent, but depends essentially upon that of the other elements with which it is associated at the moment of chemical change (see page 304; also iii. 198).

According to Meissner, ordinary oxygen is resolved by electrisation into ozone and antozone, the former of which is absorbed by iodide of potassium, pyrogallic acid, &c., while the latter remains unabsorbed. He finds that when perfectly dry electrised air is made to pass through water, white fumes are produced on its exit into the air, and that the same fumes are produced when the dry electrised air is made to flow into moist air. These fumes he regards as a mechanical mixture of antozone with aqueous vapour. According to v. Babo, however, these fumes are for the most part produced only in presence of nitrogen or oxidisable substances; he regards them as consisting

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of peroxide of hydrogen, which is known to be formed by the action of ozone on water, either in the liquid or the gaseous form. Von Babo also asserts that the proportion of ozone produced in air or oxygen by electrisation is the same whether the electricity used be positive or negative or the two alternately, a result which appears inconsistent with the production of two oppositely polarised varieties of oxygen by electrisation. Moreover ozonised air suffers no diminution in its amount of ozone by passing through a solution of permanganic acid, whereas such diminution always occurs if the air has previously been in contact with oxidisable substances, which may have given rise to the formation of peroxide of hydrogen.

### Compounds of Oxygen.—Oxides and Hydrates.

Oxygen may enter into combination in various ways, taking the place of hydrogen (in the proportion of 1 at. O to 2 at. H) in the radicles of compounds formed on either of the types, HCl, $H^2O$, $H^3N$, $H^4C$, thus giving rise to oxy-chlorides, oxy-iodides, oxy-nitrides, &c.; but the term, "oxide" is specially applied to compounds derived from a single or multiple atom of water, $H^2O$ or $nH^2O$, where part at least of the oxygen occupies the place external to the radicle. When the hydrogen in the type is partly replaced by other elements or by compound radicles, the resulting compound is a hydrate, basylous, acid or saline, according to the nature of the substituted radicles; thus KHO and $Ba''H^2O^2$ are basylous hydrates; $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, $\left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2$, and $\left.\begin{matrix}(PO)'''\\H^3\end{matrix}\right\}O^3$ are acid hydrates or acids; $\left.\begin{matrix}(SO^2)''\\KH\end{matrix}\right\}O^2$ and $\left.\begin{matrix}(PO)'''\\KH^2\end{matrix}\right\}O^3$ are saline hydrates or acid salts. If the whole of the hydrogen is replaced by one or more radicles, the resulting compound is an anhydrous oxide, basylous, acid or saline, according to the nature of the radicles which enter into its constitution; thus $K^2O$, $Ba''O$, and $\overset{'''}{Bi}{}^2O^3$ are basylous oxides; $(C^2H^3O)^2O$, $(SO^2)''O$ and $(P'''O)^2O^3$ are acid oxides, anhydrous acids, or anhydrides; $\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O$, $\left.\begin{matrix}(SO^2)''\\K^2\end{matrix}\right\}O^2$, $\left.\begin{matrix}(PO)'''\\Na^3\end{matrix}\right\}O^3$ are saline oxides or neutral salts.

It must be observed, however, that the distinctions between basic, acid and saline oxides are in great part merely conventional, inasmuch as basylous and chlorous elements or radicles, and consequently basic and acid oxides and hydrates, shade off into one another by insensible gradations, so as to preclude the possibility of drawing any strict line of demarcation between them. Still there are certain hydrates which have a marked tendency to exchange their hydrogen for a chlorous, acid, or electro-negative element or radicle, these constituting the basylous hydrates; while others have a decided tendency to exchange their hydrogen for a metallic, basylous, or electro-positive element or radicle, and these constitute the acid hydrates or acids. The chemical or electro-chemical characters of the anhydrous oxides are less marked than those of the hydrates; nevertheless some of those containing radicles of decided acid tendency unite more or less readily with those containing radicles of opposite character, the resulting compound being a salt; thus sulphuric anhydride $SO^3$, passed in the state of vapour over moderately heated anhydrous baryta $Ba''O$, unites with it readily, the combination being attended with vivid incandescence, and forms sulphate of barium $Ba''SO^4$; in like manner silicic and boric anhydrides unite readily with basylous oxides when ignited in contact with them, and expel carbonic anhydride from carbonates.

The general properties of acid hydrates and oxides have been already described in the articles ACIDS and ANHYDRIDES. We have here therefore only to speak of the composition and properties of the more basic or positive among these compounds.

### *Metallic Oxides and Hydrates.*

1. *Oxides with one atom of oxygen, formed on the type of a single atom of water*, $H^2O$. —The alkali-metals, lithium, sodium, potassium, cæsium, and rubidium, and one of the heavy metals, namely thallium,[*] which are mono- or proto-equivalent, that is capable of replacing hydrogen—atom for atom—form mono- or proto-hydrates having the general formula $M'HO$. These hydrates are soluble in water, forming strongly alkaline solutions which precipitate the solutions of all other metals, excepting the alkaline earth-metals, barium, strontium, and calcium. The hydrates of the alkali-metals volatilise slightly, but do not decompose even at the highest temperatures. Hydrate of thallium, on the other hand, becomes anhydrous when heated at 100° in the air, or left over oil of vitriol at common temperatures.

All proto-equivalent metals also form anhydrous protoxides, having the general formula $M^2O$. To this group belong also the salifiable oxides of the di-equivalent metals, included in the formula $M''O$; such are the oxides of barium, strontium, calcium, of all the other earth-metals excepting aluminium, and of many of the heavy metals, namely zinc, cadmium, chromium, manganese, iron, nickel, cobalt, uranium, copper, mercury, lead, palladium, platinum, tin, and a few others. Lastly, there are two oxides containing 4 atoms of metal to 1 atom of oxygen, viz. $Ag^4O$ and $Cu^4O$. The former has long been known; the latter was obtained by H. Rose (Bull. Soc. Chim. 1864, p. 330) by treating a cupric salt with an alkaline solution of stannous oxide. In these oxides, 2 atoms of metal take the place of 1 atom hydrogen. They are easily decomposed by acids, with separation of metal, and formation of argentic and cupric salts respectively.

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[*] Thallium in many other of its chemical relations exhibits a marked resemblance to the alkali-metals.

The protoxides of the alkali-metals and of thallium are decomposed by water, with formation of soluble hydrates (*e. g.* $K^2O + H^2O = 2KHO$); the oxides of barium, strontium, and calcium unite directly with water, also forming soluble hydrates (*e. g.* $Ba''O + H^2O = Ba''H^2O^2$). All other protoxides are insoluble, or nearly so, and are for the most part unaltered by water; the protoxides of magnesium and lead, however, are slowly converted by water into hydrates. Protoxides and protohydrates are decomposed by most acids, with formation of salts, and elimination of 1 atom of water: *e. g.*

$$\begin{array}{lcccccc} KHO & + & HCl & = & H^2O & + & KCl. \\ TlO & + & 2HCl & = & H^2O & + & 2TlCl. \\ Ba''O & + & 2HCl & = & H^2O & + & Ba''Cl^2. \\ Ba^2O & + & H^2SO^4 & = & H^2O^4 & + & Ba''SO^4. \end{array}$$

2. *Oxides and Hydrates containing two atoms of Oxygen, formed on the type of a double atom of water*, $H^4O^2$.—This group includes:—*a.* The hydrates of the di-equivalent metals, barium, calcium, lead, copper, &c., *e.g.* barytic hydrate $Ba''H^2O^2$, cupric hydrate $Cu''H^2O^2$, stannous hydrate $Sn''H^2O^2$. The hydrates of barium, strontium and calcium are soluble in water; the rest are insoluble or very slightly soluble, as hydrate of lead. All these hydrates are decomposed by heat into metallic oxide and water; but the degree of heat required to effect the change is different in each particular instance. Thus, cupric hydrate is decomposed at a temperature below that of boiling water, whereas hydrate of calcium requires a full red heat to resolve it into quicklime and water. These hydrates are decomposed by acids, with formation of salts and elimination of 2 at. water:

$$\begin{array}{lcccccc} Ba''H^2O^2 & + & 2HCl & = & 2H^2O & + & Ba''Cl^2 \\ Cu''H^2O^2 & + & H^2SO^4 & = & 2H^2O & + & Cu'SO^4. \end{array}$$

*β.* The anhydrous salifiable oxides of tetra-equivalent metals, *e. g.* zirconia $Zr^{iv}O^2$, thorina $Th^{iv}O^2$, stannic oxide $Sn^{iv}O^2$, platinic oxide $Pt^{iv}O^2$, and the corresponding oxides of the other metals of the platinum group; also titanic oxide $Ti^{iv}O^2$, tantalic oxide $Ta^{iv}O^2$, niobic oxide $Nb^{iv}O^2$, and the dioxides of molybdenum, tungsten, and vanadium. All these dioxides, excepting those of titanium, tantalum, and niobium, have more or less of a basylous character, and are converted into salts by the action of acids; but they all, excepting those of molybdenum, tungsten and vanadium, likewise exhibit the characters of acid oxides, and form salts with the more basylous oxides. In the same group of acid oxides may also be included the dioxides of certain semimetallic elements, namely silicic oxide or anhydride $SiO^2$, selenious oxide $Se^{iv}O^2$, and tellurous oxide $Te^{iv}O^2$.

*γ.* Certain double or saline oxides in which half the hydrogen is replaced by 2 atoms of a mono-equivalent, and half by 1 atom of a di-equivalent metal, such as potassium-zinc-oxide $K^2Zn''O^2$, platinite of potassium $K^2Pt''O^2$, stannite of sodium $Na^2Sn''O^2$, &c.

*δ.* In addition to the acid and basylous dioxides above mentioned, there are certain other oxides with two atoms of oxygen, possessed of very different properties. In these last dioxides, typified by peroxide of hydrogen $H^2O^2$, the second atom of oxygen seems to be retained on a very uncertain tenure. Oxides of this description are usually termed peroxides, to distinguish them from the salifiable oxides already considered. These peroxides do not form any corresponding chlorides, or corresponding salts in general, but when acted upon by hydrochloric acid, they evolve either peroxide of hydrogen or chlorine, thus:

$$\begin{array}{lcccccccc} BaO^2 & + & 2HCl & = & H^2O^2 & + & Ba''Cl^2 & & \\ MnO^2 & + & 4HCl & = & 2H^2O & + & Mn''Cl^2 & + & Cl^2. \end{array}$$

The peroxides of barium, strontium, calcium, potassium, and sodium have a tendency to produce peroxide of hydrogen; while the peroxides of the less basylous metals, manganese, lead and silver, have a tendency to produce chlorine. In accordance with these different tendencies, the alkaline peroxides are found to exert in many cases a reducing action, like peroxide of hydrogen (iii. 198), whereas the peroxides of manganese, lead and silver, act more generally as oxidising agents; and hence it has been inferred by Schönbein and others (p. 302) that the oxygen in the alkaline peroxides is essentially electro-positive, whereas that in peroxide of manganese &c. is essentially negative. These differences, however, are not really permanent and essential, but vary with the conditions under which the second atom of oxygen is set free. In the first place, all peroxides alike evolve chlorine (*i. e.* exert an oxidising action) when heated with strong hydrochloric acid.—2. An acid solution of peroxide of hydrogen converts ferrocyanide into ferricyanide of potassium, whereas an alkaline peroxide mixed with an alkaline or neutral solution of the ferricyanide reduces it to ferrocyanide.—3. An alkaline solution of peroxide of sodium added to a manganous salt forms hydrated peroxide of manganese; whereas an acid solution of peroxide of hydrogen mixed with permanganate of potassium evolves oxygen and forms a manganous salt.—4. An alkaline solution of peroxide of sodium oxidises an alkaline solution of chromic oxide, converting it into chromic acid, whereas acid solutions of peroxide of hydrogen (or of the alkaline peroxides) reduce chromic acid to chromic oxide (Brodie, Chem. Soc. J. xvi. 333; see also i. 856 and iii. 198). All peroxides, also, whether of the more or less basylous subgroups, alike yield oxygen and a protosulphate when acted upon by strong sulphuric acid:

$$BaO^2 + H^2SO^4 = H^2O + O + Ba''SO^4.$$
$$MnO^2 + H^2SO^4 = H^2O + O + Mn''SO^4.$$

The oxygen evolved from the above reaction with peroxide of barium is highly ozonic, and that from the reaction with peroxide of manganese appears to contain a trace of ozone.

These peroxides might also be classified as a distinct group, and represented by a distinct set of formulæ, thus:

| | | | |
|---|---|---|---|
| $H^2O\ .\ O$ | Peroxide of hydrogen. | $BaO\ .\ O$ | Peroxide of barium. |
| $Na^2O\ .\ O$ | Peroxide of sodium. | $MnO\ .\ O$ | Peroxide of manganese. |
| $K^2O\ .\ O$ | Peroxide of potassium. | $PbO\ .\ O$ | Peroxide of lead. |
| $CaO\ .\ O$ | Peroxide of calcium. | $Ag^2O\ .\ O$ | Peroxide of silver. |
| $SrO\ .\ O$ | Peroxide of strontium. | | |

We find, however, that although non-salifiable as a rule, yet under certain circumstances, some of these oxides can act as if salifiable. Thus the peroxides of manganese and lead are capable of dissolving in acetic acid to form diacetates. Moreover, the acknowledged salifiable dioxide of palladium manifests many of the properties of a peroxide. Whence it seems that the difference between a salifiable dioxide and a neutral peroxide is rather a difference of habit than of essential character; and this view is confirmed by a consideration of the peroxides with three atoms of oxygen belonging to the next group. Most of the above peroxides can exist in the hydrated state, but whether or not the water exists as a separate constituent has not been satisfactorily ascertained. Some oxides also, having the formulæ of $\frac{3}{4}$-oxides, have the characters of peroxides. Thus, red oxide of lead has a formula corresponding to that of black oxide of iron, but the two bodies behave very differently when treated with acids. The former breaks up in accordance with this equation:

$$Pb^3O^4 = 2Pb''O + \overset{\text{Non-salifiable.}}{PbO^2};$$

the latter in accordance with this:

$$Fe^3O^4 = Fe''O + \overset{\text{Salifiable.}}{\overset{\prime\prime\prime}{Fe}{}^2O^3}.$$

3. *Oxides with three atoms of oxygen, formed on the type of three atoms of water,* $H^6O^3$. *a.* In this class are included salifiable trioxides and trihydrates. The most basylous of the trioxides are alumina $\overset{\prime\prime\prime}{Al}{}^2O^3$, ferric oxide $\overset{\prime\prime\prime}{Fe}{}^2O^3$, chromic oxide $\overset{\prime\prime\prime}{Cr}{}^2O^3$, ceric oxide $\overset{\prime\prime\prime}{Ce}{}^2O^3$, and trioxide of bismuth $\overset{\prime\prime\prime}{Bi}{}^2O^3$. In the trioxides of gold and antimony, $\overset{\prime\prime\prime}{Au}{}^2O^3$ and $\overset{\prime\prime\prime}{Sb}{}^2O^3$ respectively, the chlorous and basylous functions are pretty equally balanced, while in trioxide of arsenic $\overset{\prime\prime\prime}{As}{}^2O^3$ the basylous character is scarcely to be recognised. This last trioxide is sparingly soluble in water, being converted by solution into its corresponding hydrate or acid, thus: $\overset{\prime\prime\prime}{As}{}^2O^3 + 3H^2O = 2H^3As'''O^3$.

The more basylous trioxides are practically insoluble in water. They all form hydrates, among which the aluminic, ferric, chromic, and ceric hydrates are represented by the general formula $H^3M'''O^3$. These normal hydrates are somewhat unstable, especially on the application of heat, whereby they lose water and are reduced to the type $HM'''O^2$. For example, $H^3Fe'''O^3$ when dried at 120° loses $H^2O$, and becomes $HFe'''O^2$. Hydrate of bismuth when first precipitated has probably also the composition $H^3Bi'''O^3$, but by drying it loses 1 at. water and is reduced to $HBi'''O^2$. By a further application of heat these hydrates are rendered anhydrous, thus:

$$2H^3Fe'''O^3 \quad - \quad 3H^2O \quad = \quad Fe^2O^3.$$

The basylous trihydrates are all readily soluble in acids. The trioxides of aluminium, iron, chromium and cerium exist in several different modifications, some of which are readily, others scarcely at all acted upon by acids. But all salifiable oxides and hydrates with three atoms of oxygen, when decomposed by acids, yield corresponding salts, and eliminate three atoms of water, thus:—

$$\overset{'''}{Bi}{}^2O^3 \quad + \quad 6HCl \quad = \quad 3H^2O \quad + \quad 2Bi'''Cl^3$$
$$H^3Al'''O^3 \quad + \quad 3HCl \quad = \quad 3H^2O \quad + \quad Al'''Cl^3.$$

*β.* Certain trioxides have the characters of peroxides; that is to say, when acted upon by acids, they do not form trisalts but protosalts, and simultaneously evolve oxygen or chlorine. The trioxides of cobalt and nickel $Co^2O^3$ and $Ni^2O^3$ respectively, are as decidedly peroxides as the dioxides of lead and barium. The trioxide of manganese is intermediate in its properties, and serves to connect the salifiable oxides of chromium and iron with the indifferent trioxides, or peroxides, of nickel and cobalt. Thus it dissolves in cold hydrochloric acid to form an unstable hydrated trichloride of manganese:—

$$Mn^2O^3 \quad + \quad 6HCl \quad = \quad 3H^2O \quad + \quad 2Mn'''Cl^3.$$

But when heated with hydrochloric acid, it forms dichloride of manganese and chlorine:—

$$Mn^2O^3 \quad + \quad 6HCl \quad = \quad 3H^2O \quad + \quad 2Mn''Cl^2 \quad + \quad Cl^2.$$

*γ.* Certain oxides with three atoms of oxygen react in a very peculiar manner with acids, as if two-thirds of the oxygen were retained by the metal on a more intimate footing than the remainder. Trioxide of uranium $U^2O^3$, is the most striking member of this class. To judge from its reactions, it would seem to be the protoxide of an oxidised radicle $U^2O^2$, playing the part of a metal. This trioxide might be represented by the formula $(U^2O^2)''O$, analogous to that of protoxide of copper $Cu''O$, in which the compound radicle $U^2O^2$ plays the part of metallic copper Cu. Certain it is that the grouping $U^2O^2$ is capable of being transferred from one compound to another in exchange for an atom of hydrogen or its representative, precisely as is the metal copper, thus:—

$$Cu''O \quad + \quad 2HNO^3 \quad = \quad H^2O \quad + \quad Cu''(NO^3)^2.$$
$$(U^2O^2)''O \quad + \quad 2HNO^3 \quad = \quad H^2O \quad + \quad (U^2O^2)''(NO^3)^2.$$

In a similar manner, the trioxide of antimony occasionally, and the trioxide of iron more rarely, react as if their respective formulæ were $(Sb^2O^2)''O$ and $(Fe^2O^2)''O$. In many aluminous silicates also, the trioxide of aluminium $Al^2O^3$, appears to function as a protoxide of aluminyl $(Al^2O^2)''O$. The peculiarity of the trioxide of uranium is that it never acts as a salifiable trioxide, but always as an oxide of uranyl. Oxides behaving in the above-described manner, were termed by Laurent basyl-oxides, and their corresponding salts basyl-salts.

4. *Oxides with four atoms of oxygen, formed on the type* $H^8O^4$. The only known anhydrous oxide belonging to this type is the tetroxide of osmium $OsO^4$ (p. 246).

The hydrates corresponding to the dioxides also belong to it: *e. g.* stannic hydrate $H^4Sn^{iv}O^4$, palladic hydrate $H^4Pd^{iv}O^4$, platinic hydrate $H^4Pt^{iv}O^4$; also certain double or saline oxides containing tetratomic metals, *e. g.* stannate of sodium $Na^4Sn^{iv}O^4$, platinate of potassium $K^4Pt^{iv}O^4$, &c.

The type $H^8O^4$ also includes the large class of oxides known as ¾-oxides, compounds in which 6 atoms of hydrogen are replaced by 2 atoms of a tri-equivalent metal, while the remaining two in the type either remain or are replaced by one atom of a di-equivalent metal. Examples of these compounds are furnished by magnetic oxide of iron $Fe''(Fe''')^2O^4$, chrome-iron $Fe''(Co''')^2O^4$, red lead $Pb''(Pb''')^2O^4$, red oxide of manganese $Mn''(Mn''')^2O^4$, &c. Some of the native ¾-oxides are very slowly attacked by acids, but all of them, when decomposed by acids, form salts corresponding to the acids, with elimination of 4 at. water for each atom of oxide decomposed; *e. g.*,

$$Fe''(Fe''')^2O^4 \quad + \quad 8HCl \quad = \quad 4H^2O \quad + \quad Fe''Cl^2 \quad + \quad 2Fe'''Cl^3.$$

*Oxides with five atoms of oxygen, formed on the type* $H^{10}O^5$. To this type belong the pentoxides of bismuth $Bi^2O^5$, antimony $Sb^2O^5$, and arsenic $As^2O^5$, all of which are of acid character. The last is easily soluble in water, the other two are insoluble. With these oxides may also be classed phosphoric anhydride $P^2O^5$, and nitric anhydride $N^2O^5$.

The same metal may give origin to many different oxides and hydrates, as instanced particularly by manganese. The protoxides and protohydrates are the most strongly basylous, and then follow the trioxides. The acid characters of the hydrates increase with the relative proportion of oxygen which they contain:—

| | | | |
|---|---|---|---|
| $H^2Mn''O^2$ | Manganous hydrate | $MnO$ | Protoxide |
| $HMn'''O^2$ | Manganic hydrate | $Mn^3O^4$ | ¾-oxides |
| $H^2Mn^{vi}O^4$ | Manganic acid | $Mn^2O^3$ | Trioxide |
| $HM^{vii}O^4$ | Permanganic acid | $MnO^2$ | Peroxide |

The relations of the principal classes of chlorides and salifiable oxides to one another are shown in the following table:—

| | *Chloride.* | | *Oxide.* |
|---|---|---|---|
| Protochloride | $KCl$ | Protoxide* | $K^2O$ |
| Dichloride | $Ba''Cl^2$ | ,, | $Ba''O$ |
| Tetrachloride | $Sn^{iv}Cl^4$ | Dioxide | $Sn^{iv}O^2$ |
| Trichloride | $Cr'''Cl^3$ | Trioxide | $Cr^2O^3$ |
| Hexchloride | $IrCl^4?$ | ,, | $IrO^3$ |

*Occurrence and formation of Metallic Oxides.* Some metallic oxides are found native. The principal of these are certain oxides of iron, namely, the trioxide $Fe^2O^3$, known as red hæmatite or oligiste; the hydrated trioxide $HFe'''O^2$, known as brown hæmatite or brownstone; the ¾-oxide $Fe''(Fe''')^2O^4$, known as magnetic iron ore, and certain oxides of manganese, namely, the peroxide $MnO^2$, known as pyrolusite, and several rarer oxides, including the trioxide or braunite $Mn^2O^3$, the hydrated trioxide or manganite $H(Mn)'''O^2$, the ¾-oxide or hausmanite $Mn''(Mn''')^2O^4$, and an oxide of peculiar composition, known as varvicite. The principal source of tin is the native dioxide $SnO^2$, or tinstone; of chromium, the native double oxide of chrome and iron, or chrome-iron; and of uranium, the native ¾-oxide $U''(U''')^2O^4$, or pitchblende. Trioxide of aluminium $Al^2O^3$, occurs native in the forms of ruby, sapphire, and corundum; and combined with oxide of magnesium in spinelle $Mg''(Al''')^2O^4$. Moreover, native alumina and native magnesia occur in the hydrated state, the former as diaspore, the latter as brucite. Native trioxides of antimony and bismuth have been occasionally met with, as have also the two oxides of copper. Dioxide of titanium is found native as rutile, brookite, and anatase.

Metallic oxides are obtained artificially by the following processes: *a*. The soluble hydrates of calcium, strontium, and barium are usually prepared by the action of water upon the anhydrous protoxides. The soluble hydrates of lithium, sodium, and potassium might be made in a similar way, but in practice they are always obtained by decomposing solutions of their carbonates, sulphates, or sulphydrates by other bases. Thus the carbonate of alkali-metal is usually decomposed by lime or baryta, the sulphate by baryta, and the sulphydrate by oxide of copper. Hydrate of barium likewise is frequently made by decomposing the sulphide or sulphydrate of barium with oxide of copper. The six soluble hydrates also result from the action of water at ordinary temperatures upon their respective metals. The insoluble salifiable hydrates are prepared by decomposing some or other of their salts, with the above soluble hydrates, or with ammonia, or in some cases with magnesia. Moreover, the carbonates of the corresponding basylous metals may be substituted for the above hydrates to precipitate those hydrated oxides which do not readily combine with carbonic anhydride to form carbonates, thus:

$$SnCl^2 + H^2O + Ca''CO^3 = Ca''Cl^2 + H^2Sn''O^2 + CO^2$$
$$2FeCl^3 + 3H^2O + 3Ca''CO^3 = 3Ca''Cl^2 + 2H^3Fe'''O^3 + 3CO^2.$$

And, in a few cases, water, especially boiling water, may be substituted for the alkali, thus:

$$Bi'''(NO^3)^3 + 3H^2O = 3HNO^3 + H^3Bi'''O^3.$$

Nitrate of tellurium is decomposed by water in a somewhat similar manner.

The hydrated peroxides are usually prepared by adding water to the anhydrous peroxides of the highly basylous metals; or by precipitating their soluble salts with peroxide of hydrogen; or by passing chlorine gas through the protoxides of the heavy metals suspended in water or alkaline liquid:

$$Cl^2 + 2KHO + 2CoO = 2KCl + Co^2O^3H^2O.$$

The protohydrates of iron and manganese absorb oxygen from the air to form their respective sesquihydrates.

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* The recent alterations in the atomic weights of the metals (iii. 957) have necessitated corresponding alterations in the nomenclature of oxides; these compounds being now called proto- (or mono-), di-, or tri-oxides, simply according to the number of oxygen-atoms which they contain, and the proto- and tri-oxides being distinguished as di- or mono-metallic, according to the number of atoms of metal associated with the oxygen: *e.g.*, $K^2O$ = dipotassic oxide; $Ba''O$, mono-barytic, or simply barytic oxide; $Cr^2O^3$ = dichromic trioxide; $CrO^3$ chromic trioxide. The dimetallic trioxides (alumina, for example) were represented according to the former system of atomic weights (i. 465) by the formula $M^4O^3$, and called sesquioxides.

β. Anhydrous oxides are frequently prepared by directly oxidising the metal. Many oxides, especially those of volatile metals, arsenic, zinc, cadmium, and mercury, for instance, are obtained by simply heating the metals in air or oxygen. Protoxide of lead, a readily fusible oxide, is made commercially by roasting the metal in a current of air. Black oxide of iron is well known in the form of smithy scales, as a product of the ignition of iron in the atmosphere; and the two oxides of copper may be made in a similar manner. Sometimes, also, metallic oxides result from the direct action of oxygen upon certain compounds of the metals. Thus arsenious oxide, and the mixed oxides of iron and copper, are prepared by roasting metallic sulphides instead of the reguline metals. Again, peroxide of silver is made by acting upon nitrate of silver with nascent oxygen evolved from the positive plate of the battery. Many oxides, procured in various ways, are converted into their higher oxides by ignition in a current of oxygen or of air, as is the case with peroxide of barium and red oxide of lead, for instance. In this direct mode of oxidation the oxygen is frequently supplied by means of some oxidising compound. Thus the oxides of tin and antimony are readily made by acting upon the respective metals, or their sulphides, with strong nitric acid; and many oxides are procured by fusing the metals, or their sulphides, with nitre. By this last method, the resulting oxides, if at all of an acid-forming character, appear in the state of potassium-salts. Many metals, especially at a red heat, are readily oxidated by water or steam.

γ. Some oxides are made, not by oxidation, but by reduction of their superior oxides. Thus, the ¾-oxide of manganese is made by igniting the peroxide. Trioxide of chromium is made by igniting chromic acid, or the chromates of the volatile metals, mercury and ammonium. Cuprous oxide is made by reducing the cupric oxide with metallic copper. Dioxide of tungsten is made by reducing tungstic anhydride in a current of hydrogen. Sometimes the hydrogen resulting from the decomposition of ammonia effects the reduction. In this way the ignition of molybdate of ammonium yields protoxide of molybdenum.

δ. One of the most common methods of preparing anhydrous metallic oxides consists in heating metallic hydrates, carbonates, oxalates, nitrates, and sulphates. Nearly all metallic hydrates yield metallic oxide by exposure to a degree of heat varying from below 100° to full redness. The hydrates of potassium, sodium, and lithium are not decomposed by heat, but can yield their corresponding oxides by treatment with their respective metals: $NaHO + Na = Na^2O + H$. All metallic carbonates, excepting those of barium, potassium, sodium, and, to some extent, lithium, are decomposed by heat and yield metallic oxide. Quicklime or protoxide of calcium is made in this way by the ignition of chalk or carbonate of calcium. The oxides of nickel and cobalt are frequently prepared by igniting their oxalates; those of barium, copper, and mercury by igniting their nitrates; and those of iron and aluminium, by igniting their sulphates.

Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. With the exception of the peroxides of silver, lead, and manganese, they are non-conductors of electricity. The densities of metallic oxides, save of the highly basylous ones, are usually lower than those of the metals themselves. Some native oxides are extremely hard. This hardness greatly exceeds, but otherwise bears no relation to, the hardness of the corresponding metals. At ordinary temperatures, all metallic oxides occur in the solid state. The majority of them are fusible, those of lead and bismuth at a low red heat, those of copper and iron at a white heat, those of barium and aluminium in the oxyhydrogen blowpipe, but that of calcium at no temperature to which it has hitherto been subjected. Unlike the compounds of metal with chlorine, which are much more fusible, the compounds of metals with oxygen, except indeed the black oxide of iron, the trioxide of chromium, and the trioxide of molybdenum, are much less fusible than the uncombined metals. Tetroxide of osmium, the trioxides of arsenic and antimony, and the dioxide of tellurium are readily volatile.

A greater or less degree of heat effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the reguline state by an incipient red heat. At a somewhat higher temperature, the peroxides of barium, cobalt, nickel and lead are reduced to the state of protoxides; while the the ¾-oxides of manganese and iron result from the exposure of the dioxide and trioxide respectively to a still stronger degree of heat. By gentle ignition arsenic anhydride is reduced to the state of arsenious anhydride, and chromic anhydride to the state of trioxide of chromium.

The superior oxides of the metals are readily reduced to a lower state of oxidation by treatment with a current of *hydrogen gas* at a more or less elevated temperature. At a higher degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the trioxides of aluminium and chromium, and the protoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus even metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness, so as to form an iron pyrophorus. *Carbon*, at a red or white heat, is a still more powerful deoxidating agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. In the reduction of metallic oxides by carbon at a high temperature, carbonic oxide is always produced, the reducing power of which gas also is extremely great. The *oxidisable metals* in general act as reducing agents. As a rule, the more basylous metals, when heated with the oxides of less basylous metals, reduce the latter to the reguline state. Many inferior oxides, cuprous oxide for instance, are made by reducing the higher oxides with metal.

With the exception of the oxides of the earth-metals, *chlorine* decomposes all metallic oxides, uniting with the metals to form chlorides, and expelling the oxygen. With oxide of silver this reaction takes place at ordinary temperatures; with the alkalis and alkaline earths, at a full red heat. The action of chlorine upon metallic hydrates and moist metallic oxides, to form metallic chlorides and either hypochlorites or peroxides, has been already described.

*Sulphur* at an elevated temperature can decompose most metallic oxides. With many oxides, those of silver, mercury, lead and copper, for instance, metallic sulphides and sulphurous anhydride are produced. With the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromic oxide, and the stannic and titanic anhydrides. By boiling sulphur with soluble hydrates, mixtures of polysulphide and hyposulphite are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or sulphydrate and water.

The action of *phosphorus* upon metallic oxides is very analogous to that of sulphur; it usually produces a mixture of phosphide and phosphate. Like sulphur it does not react with magnesia or alumina. Boiled with the soluble alkalis it produces phosphoretted hydrogen and a hypophosphite.

The action of *water* and *acids* upon metallic oxides has been already considered (pp. 302–306). Many of the acid oxides dissolve in water to a greater or less extent, undergoing decomposition and forming acid solutions. But the dioxides of tin, titanium, zirconium, and tantalum, and the trioxides of tellurium and tungsten, may be obtained in a state perfectly insoluble in water. (*Odling's Manual of Chemistry*.)

### *Peroxides of Organic Radicles.*

The hydrates and oxides of basylous or positive organic radicles formed on the $n.H^2O$ have been already described under ALCOHOLS (i. 97) and ETHERS (ii. 508); the hydrates and oxides of acid or negative organic radicles formed on the same type are described under ACIDS (i. 39), and ANHYDRIDES (i. 293). We have here to describe certain peroxides of acid organic radicles recently discovered by Brodie (Proc. Roy. Soc. ix. 361, xii. 655; Phil. Trans. 1864, p. 407; Chem. Soc. J. xvii. 266). The following have been obtained:—

| | | | |
|---|---|---|---|
| Peroxide of Acetyl . . . | $C^4H^6O^4$ | = | $(C^2H^3O)^2.O^2$ |
| Peroxide of Butyryl . . . | $C^8H^{14}O^4$ | = | $(C^4H^7O)^2.O^2$ |
| Peroxide of Valeryl . . . | $C^{10}H^{18}O^4$ | = | $(C^5H^9O)^2.O^2$ |
| Peroxide of Benzoyl . . . | $C^{14}H^{10}O^4$ | = | $(C^7H^5O)^2.O^2$ |
| Peroxide of Nitrobenzoyl . . | $C^{14}H^8(NO^2)^2O^4$ | = | $[C^7H^4(NO^2)O]^2.O^2$ |
| Peroxide of Cuminyl . . | $C^{20}H^{22}O^4$ | = | $(C^{10}H^{11}O)^2.O^2$ |
| Peroxide of Camphoryl . . | $C^{10}H^{14}O^4$ | = | $C^{10}H^{14}O^2.O^2$. |

These organic peroxides are produced by the action of peroxide of barium on the chlorides or oxides (anhydrides) of the several acid radicles. In their chemical relations they are the analogues of peroxide of hydrogen and of chlorine.

The formulæ just given express their composition in the free state; the first six, which contain monatomic radicles, might all be halved, but the half-formulæ would contain uneven numbers of hydrogen-atoms and cannot therefore be admitted for the isolated compounds: these half-molecules, however, like the single atom of chlorine, may exist in combination with hydrogen, producing the corresponding acids; thus:—

| Free chlorine. | Hydrochloric acid. |
|---|---|
| ClCl. | HCl. |
| Free peroxide of acetyl. | Acetic acid. |
| $C^4H^6O^4$. | $H.C^2H^3O^2$. |

*Peroxide of Acetyl*, $C^4H^6O^4$, is prepared by dissolving acetic anhydride in pure ether, and gradually adding an equivalent quantity of pure peroxide of barium:

$$2C^4H^6O^3 \quad + \quad Ba''O^2 \quad = \quad C^4H^6Ba''O^4 \quad + \quad C^4H^6O^4.$$

Its preparation and properties have already been described (i. 35). When dry it is violently explosive and must be handled with the greatest caution. It is a powerful oxidising agent, like peroxide of hydrogen, but is distinguished from that compound by not reducing chromic or permanganic acid in acid solution.

*Peroxide of Butyryl*, $C^8H^{14}O^4$, is easily prepared by carefully mixing butyric anhydride with an equivalent quantity of hydrated peroxide of barium (till a drop of the mixture, acidulated with hydrochloric acid, gives a faint blue colour with dilute solution of acid chromate of potassium), stirring up the mass with a little water, and agitating with ether. The ethereal solution washed with dilute hydrochloric acid, carbonate of sodium, and water, and left to evaporate, leaves the peroxide of butyryl as an oily body only slightly soluble in water; it must be dried with chloride of calcium. It decomposes with slight explosion when heated, and when suspended in water exerts an oxidising action, like the acetyl-compound.

*Peroxide of Valeryl*, $C^{10}H^{18}O^4$, prepared in like manner, is a heavy oily liquid, possessing similar properties.

*Peroxide of Benzoyl*, $C^{14}H^{10}O^4$, is prepared by gradually mixing pure hydrated peroxide of barium (previously dried by pressure between bibulous paper) in a mortar with an equivalent quantity of chloride of benzoyl; mixing the mass after some hours with water; washing it on a filter with water to remove chloride of barium, then with carbonate of sodium to remove benzoic acid; drying the product under the air-pump, and crystallising it several times from sulphide of carbon, which must not be heated above 35°. The quantity thus obtained amounts to about 88 per cent. of the benzoic chloride used. Excess of water diminishes the product. It is necessary, however, to use hydrated peroxide of barium, because the anhydrous peroxide does not act upon benzoic anhydride, or chloride of benzoyl dissolved in ether, even at 100°. The quantity of the product is also diminished by the presence of peroxide of barium in excess, inasmuch as this body, in presence of water, destroys the peroxide of benzoyl, exerting a reaction exactly opposite to that by which it was produced: thus,

$$\text{Formation:}\quad \underset{\substack{\text{Benzoic}\\ \text{chloride.}}}{2C^7H^5OCl} + BaO^2 = BaCl^2 + \underset{\substack{\text{Benzoic per-}\\ \text{oxide.}}}{(C^7H^5O)^2O^2}.$$

$$\text{Decomposition:}\quad \underset{\substack{\text{Benzoic per-}\\ \text{oxide.}}}{(C^7H^5O)^2O^2} + BaO^2 = \underset{\substack{\text{Benzoate of}\\ \text{barium.}}}{(C^7H^5O)^2Ba''O^2} + O^2.$$

Peroxide of benzoyl may be obtained in large splendid crystals, belonging to the trimetric system, and exhibiting the combination $\infty P \,.\, oP \,.\, P \,.\, \breve{P}\infty \,.\, \frac{1}{2}\bar{P}\infty \,.\, \frac{1}{3}\bar{P}\infty$. Inclination of the faces, $\breve{P}\infty : oP = 146° 36'$; $\infty P : \infty P = 115° 41'$; $\frac{1}{2}\bar{P}\infty : \frac{1}{2}\bar{P}\infty = 124° 39'$; $\frac{1}{3}\bar{P}\infty : \frac{1}{3}\bar{P}\infty = 143° 30'$; $\breve{P}\infty : \breve{P}\infty$ over the principal axis $= 113° 12'$; $P : P$ in the brachydiagonal terminal edge $= 131° 4'$; in the macrodiagonal terminal edge $= 97° 36'$; at the base $= 102° 11'$. (Müller.)

Peroxide of benzoyl melts at 103·5° (only very small quantities, however, can be melted without decomposition); it dissolves readily in ether and benzene, and in 39·5 pts. sulphide of carbon at 15°. It is decomposed by boiling potash-ley with evolution of oxygen, and formation of potassic benzoate. When heated alone it decomposes with slight explosion; if mixed with sand, it gives off carbonic anhydride (nearly 18 per cent.), at about 85°, leaving a resinous substance.

*Peroxide of Nitrobenzoyl*, $C^{14}H^8(NO^2)^2O^4$, is precipitated on adding water to a solution of benzoic peroxide in a large excess of fuming nitric acid, and remains, on evaporation of its solution, in sulphide of carbon, as a light yellow substance which decomposes with slight explosion when heated.

*Peroxide of Cuminyl*, $C^{20}H^{22}O^4$, is prepared like the benzoyl-compound, and crystallises from ether in long needles, which explode when heated, leaving a resinous substance.

*Peroxides of Diatomic Acid Radicles.* The anhydrides of dibasic acids treated with peroxide of barium form easily decomposible compounds which may be regarded as the peroxides of diatomic radicles. When *succinic anhydride* is gradually mixed with peroxide of barium and a little water, an evolution of oxygen soon takes place, and an alkaline liquid is formed which does not contain any succinate of barium, but possesses strong oxidising properties, though it contains no peroxide of hydrogen, as it does not decolorise permanganic acid or form a blue colour with acid chromate of potassium (as is the case with a mixture of barium-peroxide and succinic acid). The solution bleaches indigo, precipitates manganic peroxide from manganous acetate, oxidises ferrocyanide of potassium, eliminates chlorine from hydrochloric acid when heated with it, and is resolved by boiling into free oxygen and succinate of barium. With *lactide* a solution is formed possessing similar properties, but still more decomposible. More permanent is the alkaline strongly oxidising solution obtained by saturating 1 at. *camphoric anhydride* in a well-cooled vessel, with 1 at. barium-peroxide and water. This solution appears to contain the barium-salt of camphoric peroxide $C^{10}H^{14}Ba''O^5$, formed by the direct union of camphoric anhydride $C^{10}H^{14}O^3$ with barium-peroxide $BaO^2$, and not a camphorate of barium-peroxide; for it does not yield peroxide of hydrogen with acids, or barium-peroxide with alkalis.

**OXYGEN, DETECTION AND ESTIMATION OF.** Oxygen in the pure state, is easily distinguished from all other gases by the facility with which it supports combustion; a taper or a piece of wood immersed in it with only a single point in a state of ignition bursts instantly into flame. This effect is not produced by any other gas except nitrous oxide, which acts like diluted oxygen, rekindling the taper only when the wick is still in a state of vivid glow.

In gaseous mixtures, oxygen may be detected, and its quantity estimated, by means of a solution of *pyrogallate of potassium*, which absorbs it rapidly, turning black at the same time; for the details of the method see ANALYSIS OF GASES (i. 283). A solution of *gallic* or *tannic acid* in excess of potash may also be used; but the action of these solutions is much slower. Oxygen is also absorbed by *phosphorus, potassium*, solutions of *alkaline sulphides, ferrous salts*, and by an *ammoniacal solution of cuprous* chloride, or of *cuprous sulphate;* but none of these reagents are so convenient or so exact in their indications as pyrogallate of potassium.

Oxygen may also be separated from gaseous mixtures, and quantitatively estimated by explosion with *hydrogen*, the volume of oxygen present being equal to a third of the volume of gas which disappears, supposing of course that all other gases which can unite either with the oxygen or with the hydrogen have been previously removed (i. 285).

The amount of oxygen in solid or liquid compounds is usually estimated by difference, after all the other elements present have been determined (see ANALYSIS, ORGANIC, i. 239). There are but few compounds from which oxygen can be separated in the free state by the action of heat alone, and it is only from the noble metals that it can be completely separated in this way; but the usual method of determining the oxygen in metallic oxides is by ignition in an atmosphere of hydrogen, the water produced being absorbed by chloride of calcium, and weighed.

Active oxygen or ozone is distinguished from ordinary oxygen by its more powerful oxidising properties. The reagent usually employed for detecting its presence in the air, or in any gaseous mixture, is paper covered with starch-paste containing iodide of potassium, which when moistened quickly assumes a blue or violet colour in contact with ozone.

Starch-paper impregnated with solution of potassium-iodide of known strength is also used for determining the relative quantities of ozone in the air in different localities, and at different times, the amount present being regarded as inversely proportional to the time of exposure required to produce a given depth of tint. But the indications thus afforded are uncertain, the rapidity of the action being modified by various circumstances, as by the temperature and humidity of the air; moreover, the paper once coloured by ozone becomes decolorised again by continued exposure, and the same effects of coloration and subsequent decoloration may be produced by other gases in the air, chlorine, the oxides of nitrogen for example. For these reasons, Houseau prefers litmus-paper, slightly reddened and impregnated with iodide of potassium. This paper turns blue in presence of ozone, the coloration arising from the production of a certain quantity of potash and separation of iodine. The same change of colour is not produced by any other gas except ammonia, and the blueing produced by this reagent is easily distinguished from that arising from the action of ozone, inasmuch as it is likewise produced on red litmus-paper not containing iodide of potassium. Chlorine, bromine, iodine, nitrous compounds and acetic acid, change the red colour of the prepared paper to reddish yellow.

Andrews estimates the quantity of ozone contained in a given volume of air by passing the dry air through a bulb-apparatus containing solution of potassium-iodide, then through another containing strong sulphuric acid to absorb the water carried away from the first solution. The increase of weight of the two apparatus gives the quantity of ozone absorbed, and on determining the quantity of iodine set free, according to Bunsen's method (i. 265), it is found that the quantity of oxygen equivalent to the iodine thus liberated is exactly equal to that of the ozone absorbed (p. 301).

*Atomic weight of Oxygen.*—The proportion between the atomic weights of oxygen and hydrogen is determined by the analysis and synthesis of water. The most exact method consists in passing perfectly pure hydrogen gas over red-hot oxide of copper, and comparing the loss of weight which this oxide sustains with that of the water produced. Experiments made in this manner by **Berzelius** and **Dulong**, Ann. Ch.

Phys. lxv. 386), subsequently with greater exactness by **Dumas** and **Stas** (Ann. Ch. Phys. [3] viii. 189), and by **Erdmann** and **Marchand** (J. pr. Chem. xlvi. 461), concur in showing that water is composed of 1 pt. by weight of hydrogen and 8 of oxygen (iii. 195), and therefore, that if the atomic weight of hydrogen be taken as the unit, and the composition of water be represented by the formula $H^2O$, the atomic weight of oxygen is 16. The reasons for regarding water as $H^2O$, and not as $HO$, have been fully discussed in the article ATOMIC WEIGHTS (i. 461).

**OXYGENATED WATER.** Water holding peroxide of hydrogen in solution (iii. 197). **Schönbein** (J. Pharm. [4] i. 75; Bull. Soc. Chim. 1865, i. 69) detects the presence of peroxide of hydrogen in water by its power of converting the protoxides of lead, nickel and a few other metals into peroxides, and the decomposition of potassium-iodide by these peroxides in presence of an acid. The liquid to be tested having been rendered alkaline by a little potash, a small quantity of a lead-salt is added (not in excess) and then iodide of potassium mixed with starch. If then, on adding an acid, a blue colour is produced, the presence of peroxide of lead, and consequently of peroxide of hydrogen, in the original liquid may be inferred.

**OXYGENOÏD.** A name applied by **Duflos** to those non-metallic elements which in their chemical relations exhibit a certain resemblance to oxygen, viz. bromine, chlorine, fluorine, iodine, selenium and sulphur.

**OXYGUANINE.** A substance produced by the action of permanganate of potassium on guanine dissolved in caustic soda. (See GUANINE, ii. 952.)

**OXYGUMMIC ACID.** $C^4H^{10}O^{11}$. (A. **Beyer**, Ann. Ch. Pharm. cxxxi. 353.)—When glucose is treated with cupric oxide and potash for the preparation of Reichardt's gummic acid (ii. 956), the resulting liquid precipitated with chloride of barium after being rendered slightly alkaline by ammonia, and the precipitated gummate of barium dried over the water-bath, part of it is converted by oxidation into oxygummate and carbonate of barium:

$$\underset{\text{Gummic acid.}}{C^6H^{10}O^{10}} + O^5 = \underset{\substack{\text{Oxygummic}\\\text{acid.}}}{C^4H^{10}O^{11}} + 2CO^2$$

The barium-salt treated with sulphuric acid yields a solution, from which oxygummic acid may be obtained in shining needles soluble in water and alcohol. The solutions are strongly acid. The crystals dried in the air, or over sulphuric acid, give off water and leave a white powder soluble in water. Heated above 130° the acid decomposes with intumescence, giving off pungent aromatic vapours and leaving an acid carbonaceous residue.

Oxygummic acid is tetrabasic. The *barium-salt*, $C^4H^6Ba''O^{11}$, is a bulky precipitate which soon becomes crystalline; it dissolves sparingly in water, easily in hydrochloric acid, and gives off a little water at 100°. The *silver-salt*, $C^4H^6Ag^4O^{10}$, is a white precipitate sparingly soluble in acetic acid, less sensitive to light than the gummate. At 100° it deflagrates like oxalate of silver.

**OXYHIPPURIC ACID.** $C^9H^9NO^4$.—This is probably the composition of an easily soluble acid produced by boiling the aqueous solution of diazohippuric acid, $C^9H^7N^3O^3$ (the product of the action of nitrous acid on amido-hippuric acid, iii. 160). (P. **Griess**, Jahresb. 1862, p. 260.)

**OXYHYDROGEN BLOWPIPE.** See BLOWPIPE (i. 616).—**Deville** and **Debray** (Ann. Ch. Phys. [3] lvi. 385) employ the oxyhydrogen blowpipe in the following manner for effecting the fusion of platinum and the refractory metals which accompany it. The apparatus consists of the blowpipe *C* (fig. 733), a furnace *ABD*, and a crucible *GHI*. The blowpipe is composed of a copper tube about half an inch in diameter, terminating below in a slightly conical platinum jet about 1½ inch long. Within this tube, which is supplied with hydrogen or coal gas through the stop-cock *H*, is a second copper tube *C'* for supplying oxygen, terminated also by a platinum nozzle with an aperture of about a twelfth of an inch in diameter.

The furnace *ABD* consists of three pieces of well-burnt lime of slightly hydraulic quality, which may be turned at a lathe with ease. The cylinder *A* is about 2½ inches thick, and is perforated by a slightly conical hole into which the blowpipe fits accurately, passing about half-way through the thickness of the mass. A second somewhat deeper cylinder of lime *B*, is hollowed into a chamber wide enough to admit the crucible, and leave an interval of not more than a sixth of an inch clear around it. *KK* are four apertures for the escape of the products of combustion.

The outer crucible *HH* is also made of lime, but it contains a smaller crucible *I* of gas-coke, provided with a cover of the same material; and in this the substance to be fused is placed, the crucible resting on the lime support *D'*. The conical cover *G* is made of lime, and its apex should be placed exactly under the blowpipe jet, at a distance from it of ¾ to 1½ inch.

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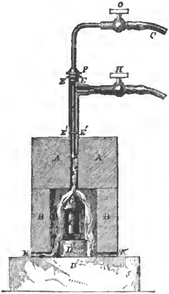
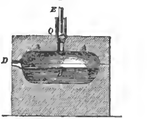
The different pieces of the furnace must be bound round with iron wire to suppor them when they crack. The oxygen is admitted under a pressure of a column of 16 inches of water. The temperature is gradually raised to the maximum, and in about eight minutes from this time the operation is complete.

Fig. 733.



By employing a jet of mixed coal-gas and oxygen (*EQ*, fig. 734) in a furnace of lime, Deville and Debray succeeded, at an expense of about 43 cubic feet of oxygen, in melting and refining in 42 minutes, 25·4 lbs. avoirdupois of platinum, and casting it into an ingot in a mould of gas-coke; and much larger masses have since been melted by this method. Lime is so bad a conductor of heat that if a cup of lime not more than 0·8 inch thick be filled with melted platinum the exterior scarcely rises beyond 300° F. (*Miller's Elements of Chemistry*, 3rd. ed. pt. ii. p. 825.)

Fig. 734.



**OXY-IODIC ACID.** Syn. with Periodic Acid.

**OXYLISATION.** A term applied by Schönbein (Pogg. Ann. lxxx. 520) to the oxidising action of nitrous acid, nitric acid, &c., at ordinary temperatures. He supposes that part of the oxygen in these bodies is in a peculiar active state (combined ozone in fact, and calls it "oxylised oxygen."

**OXYLIZARIC ACID.** Syn. with Purpurin.

**OXYMETHYL-CARBONIC ACID.** A name applied by Kolbe (Ann. Ch. Pharm. cxxvii. 159) to glycollic acid, regarded as $HO,\ C^2\left\{\begin{matrix}H^2\\ HO^2\end{matrix}\right\}[C^2O^2]O$.

**OXYMETHYL-TRIETHYL-PHOSPHONIUM.** (See Phosphorus-bases.)

**OXYMORPHINE.** According to Schützenberger (Ann. Ch. Pharm. cvii. 346), morphine ($C^{17}H^{19}NO^3$) treated with nitrous acid yields three basic products to which he assigns the formulæ, $C^{17}H^{19}NO^4$; $C^{17}H^{21}NO^4.H^2O$; and $C^{17}H^{21}NO^5$.

**OXYNAPHTHALIC ACID.** $C^{10}H^6O^3$.—This compound has not been actually obtained, but two chlorinated acids are known which may be regarded as derivatives of it, namely, chloroxynaphthalic acid $C^{10}H^5ClO^3$, and perchloroxynaphthalic acid $C^{10}HCl^5O^3$. These acids are produced by the action of potash on the corresponding chlorides (*vid. inf.*). Alizarin has the composition of oxynaphthalic acid, but it is not produced by the action of sodium-amalgam or of the electric current on chloroxynaphthalic acid.

*Chloroxynaphthalic acid*, $C^{10}H^5ClO^3$, also called *chloronaphthisic* and *chloronaphthalic acid*, has been already described under the last name (p. 14).

*Perchloroxynaphthalic acid*, $C^{10}HCl^5O^4$. Chloride of perchloroxynaphthyl treated with potash is immediately converted into a crimson substance from which acids separate yellow perchloroxynaphthalic acid. It may be crystallised from ether, converted into a potassium-salt, reprecipitated by an acid, and further purified by crystallisation from alcohol or ether. In contact with potash or ammonia it forms red or crimson salts, which are insoluble in cold water, but appear to be slightly soluble in boiling water. They may be obtained in the crystalline form by neutralising a boiling alcoholic solution of the acid with an alkali. (Laurent, Rev. Scient. xiii. 596.)

**OXYNAPHTHYL, CHLORIDE OF.** The chloride corresponding to oxynaphthalic acid has not been obtained, but two chlorinated derivatives of it, being the chlorides corresponding to the chloroxynaphthalic acids just described, were discovered by Laurent (Ann. Ch. Phys. [2] lxxiv. 35; Rev. Scient. xiii. 591). They are formed by the action of nitric acid on certain chlorinated derivatives of naphthalene.

*Chloride of Chloroxynaphthyl*, $C^{10}H^4Cl^2O^2 = C^{10}H^4ClO^2.Cl$. *Oxichloronaphtalose. Oxyde de chloroxénaphtose.*—Tetrachloride of chloronaphthalene is slowly attacked by boiling nitric acid, becoming yellow and continually more fusible. If the action be stopped as soon as the yellow substance remains on cooling in the form of a very thick oil, a solution of phthalic acid is obtained, together with a viscid yellow oil in which a yellow pulverulent deposit forms after a while. The separation of this substance may be accelerated by pouring ether on the oil, and if the ethereal solution be decanted after a day or two, the deposit washed on a filter with ether, and then dissolved in a large quantity of boiling alcohol, the solution deposits on cooling needle-shaped crystals of chloride of chloroxynaphthyl.

This compound is yellow, insoluble in water, very slightly soluble in alcohol and ether, whence it is deposited in needles. It distils without alteration; is dissolved with mahogany colour by strong sulphuric acid; and is converted by nitric acid into phthalic acid. An alcoholic solution of potash colours it crimson, and decomposes it into chloride and chloroxynaphthalate of potassium.

*Chloride of Perchloroxynaphthyl.* $C^{10}Cl^6O^2 = C^{10}Cl^5O^2.Cl$. *Oxyde de chloroxénaphtalise.*—Produced by the action of boiling nitric acid on hexchloronaphthalene. The action is very slow, requiring three or four days boiling to complete it; but ultimately a resinous substance is obtained; which, when freed from a little oily matter by ether, and purified by one or two crystallisations from boiling petroleum, has the composition of chloride of perchloroxynaphthyl.

This substance when pure forms highly lustrous golden-yellow scales. It is insoluble in *water* and *alcohol*, slightly soluble in boiling *ether*. It melts at a somewhat high temperature and volatilises in great part without alteration. By boiling *nitric acid*, it is probably converted into trichlorophthalic acid. *Potash* and *ammonia* convert it into chloride and perchloroxynaphthalate.

**OXYNAPHTHYLAMINE.** $C^{10}H^9NO$. *Oxynaphthylidine. Naphthameine.* (Piria, Ann. Ch. Pharm. lxxviii. 41.—H. Schiff, *ibid.* ci. 90.)—A base produced by the action of various oxidising agents, such as ferric, auric, mercuric, stannic, or zinc chloride, silver-nitrate, or chromic acid on naphthylamine. The violet colour acquired by naphthylamine and its salts, as well as by the thionaphthamates, on exposure to the air, is probably due to the formation of this base. According to Ganahl (Ann. Ch. Pharm. xcix. 240), it is likewise formed, with evolution of nitrogen by the first action of nitrous acid on naphthylamine suspended in water.

To prepare it, hydrochlorate of naphthylamine is dissolved in alcohol, the solution diluted with water, but not sufficient to cause turbidity, and while the whole is continuously stirred, aqueous ferric chloride is added, drop by drop, until a slight excess is present. The whole is allowed to stand for an hour with repeated stirring, and the precipitate is then collected, and washed, first with water till the wash-waters cease to become turbid with nitrate of silver, afterwards with alcohol, and then dried in vacuo (Piria). Schiff adopts the same method, or he precipitates sulphate or acetate of naphthylamine with aqueous chromic acid.

Oxynaphthylamine is a light, amorphous, dark purple powder closely resembling orceïn. When moist, it has a peculiar odour, resembling that of iodine, especially if heated. It is insoluble in *water*, also in *ammonia* and *caustic potash*. It dissolves sparingly in *alcohol*, imparting its colour to the liquid; abundantly, with purple colour, in *ether*, and is precipitated from the solution by spontaneous evaporation as an amorphous powder. It dissolves in cold *sulphuric acid*, forming a blue liquid of the colour of indigo-solution, and is precipitated by water unchanged. It dissolves in concentrated *acetic acid* with violet colour; the solution is not precipitated by water or by tartaric acid, but oxynaphthylamine is precipitated therefrom by most acids, alkalis, and metallic chlorides. (Piria.)

It does not combine with acids or with bases.

It melts when heated, and immediately decomposes, evolving an aromatic vapour smelling of naphthylamine; and finally leaves a residue of difficultly combustible charcoal, which however may be completely burned. When moist, or immersed in water, it rapidly becomes violet; hence it is difficult to obtain the dry product of a pure blue colour.

The name *oxynaphthylamine* is also applied by Dusart to a weak base, probably containing $C^{16}H^{11}NO^3$, produced by the action of reducing agents on nitroxynaphthalic acid (p. 118).

**OXYPARATARTARIC ACID.** $C^5H^8O^5 = \left.\begin{matrix}H\\(C^5H^5O^2)'''\\H^2\end{matrix}\right\}O^3$. (Maxwell Simpson, Proc. Roy. Soc. xiii. 44;—Bull. Soc. Chim. iii. 368.)—This acid, homologous with malic acid ($C^4H^6O^5$), and related to paratartaric acid in the same manner as malic to succinic acid, is produced together with ammonia by the action of potash on glycero-hydric oxydicyanide or dicyanhydrin $\left.\begin{matrix}(C^3H^5)'''\\H\end{matrix}\right\}\begin{matrix}O\\Cy^2\end{matrix}$, the cyanic analogue of dichlorhydrin:

$$C^3H^6OCy^2 + 2KHO + 2H^2O = C^5H^6K^2O^5 + 2NH^3.$$

*Preparation.*—A mixture of 1 at. dichlorhydrin and 2 at. pure potassium-cyanide with a certain quantity of alcohol is heated to 100° in well closed sedletz-water bottles for twenty-four hours, by which time the whole of the cyanide of potassium is converted into chloride. The contents of the bottles are then filtered; the solution containing dicyanhydrin is heated with sticks of potash as long as ammonia continues to escape; and the residue, after being freed from alcohol by distillation, is treated with nitric acid, the excess of which is then also evaporated off. On treating the residue consisting of potassium-nitrate and oxyparatartaric acid with alcohol, evaporating the filtrate, redissolving the strongly coloured residue in hot water and treating it with chlorine, then neutralising the whole, cautiously precipitating a third of the acid with silver-nitrate, then filtering, and precipitating the filtrate completely with silver-nitrate, a perfectly colourless silver-salt is obtained, which, when decomposed by sulphydric acid, yields oxyparatartaric acid as a colourless crystalline mass.

Oxyparatartaric acid has a pure acid taste, and dissolves in water, alcohol and ether. It melts at about 135°, and decomposes at a higher temperature. The free acid yields a copious white precipitate with acetate of lead, but is not precipitated by lime-water. When neutralised by an alkali, it gives a white precipitate with mercuric chloride, pale brown with ferric chloride, bluish-white with cupric salts, and a cloud with chloride of barium.

Oxyparatartaric acid is dibasic, the formula of its *silver-salt* being $C^5H^6Ag^2O^5$. The *ethylic ether*, $C^5H^6(C^2H^5)^2O^5$, distils between 295° and 300°, with partial decomposition.

The reaction by which this acid is obtained would, if applied to each of the cyanides derivable from diatomic and triatomic alcohols, yield for each diatomic alcohol two, and for each triatomic alcohol three acids of different degrees of basicity, thus:

*Diatomic Alcohol* (*glycol*).

| | | Cyanide. | Acid. | |
|---|---|---|---|---|
| Glycolic Chlorhydrin | $C^2H^5OCl$ | $C^2H^4OCy$ | $C^3H^6O^3$ | lactic (monobasic). |
| Dichloride of Ethylene | $C^2H^4Cl^2$ | $C^2H^4Cy^2$ | $C^4H^6O^4$ | succinic (dibasic). |

*Triatomic Alcohol* (*glycerin*).

| | | Cyanide. | Acid. | |
|---|---|---|---|---|
| Chlorhydrin . | $C^3H^7O^2Cl$ | $C^3H^7O^2Cy$ | $C^4H^8O^4$ | (monobasic). |
| Dichlorhydrin . | $C^3H^6OCl^2$ | $C^3H^6OCy^2$ | $C^5H^8O^5$ | oxyparatartaric (dibasic). |
| Trichlorhydrin . | $C^3H^5Cl^3$ | $C^3H^5Cy^3$ | $C^6H^8O^6$ | (tribasic). |

**OXYPHENIC ACID.** $C^6H^6O^2$. *Pyrocatechin. Pyromorintannic acid.* (Reinsch, *Repert.* lxviii. 54.—Wackenroder, Ann. Ch. Pharm. xxxvii. 327.—Zwenger, *ibid.* xxxvii. 327.—R. Wagner, J. pr. Chem. lii. 450; lv. 65.—Eissfeldt, *ibid.* xcii. 101.—Buchner, *ibid.* xcvi. 186.)—A substance metameric with hydroquinone (iii. 213), produced by the dry distillation of catechin, morintannic acid, and probably also of peucedanin and of kino; also of wood, whence it is found in wood-vinegar. It does not occur in coal-tar. According to Eissfeldt and Uloth (Ann. Ch. Pharm. cxi. 215), all those kinds of tannin which turn ferric salts green,—*e. g.* the tannin of *Krameria triandra, Tormentilla erecta, Polygonum Bistorta, Vaccinium Myrtillus, Pyrola umbellata, Calluna vulgaris, Ledum palustre,* &c., yield oxyphenic acid by dry distillation, whereas those kinds which turn ferric salts blue (*e. g* that of *Arbutus Uva Ursi,* and of *Rhododendron ferrugineum*) do not yield it. It is also produced, together with carbonic anhydride, by heating oxysalicylic acid to 210°—212°: $C^7H^6O^4 = CO^2 + C^6H^6O^2$, a certain quantity of the metameric body hydroquinone being always formed at the same time. Iodophenylic acid treated with potash-ley also yields oxyphenic acid. (Lantemann, Ann. Ch. Pharm. cxx. 299.)

*Preparation.*—1. Catechin or catechu is introduced into a capacious retort and quickly heated above its melting point till it chars; the distillate which collects in the cooled receiver is evaporated at 30° till crystals form on the surface, the empyreumatic oils which become resinised during the evaporation being separated by filtration; the black-brown crystalline mass which forms on cooling is sublimed (after pressure between paper, according to Wagner), a large quantity of liquid then passing over at first, which also yields oxyphenic acid by evaporation; and the sublimation of the crystals is repeated three or four times, till they no longer become coloured on exposure to the air (Zwenger).—2. Crude morintannic acid mixed with an equal quantity of sand is heated in a retort over a moderate fire; and the distillate, which solidifies on cooling, is freed from oil containing phenol by pressure between paper, and purified by sublimation and recrystallisation from water (Wagner).—3. Malabar kino or butea-kino yields by dry distillation a clear watery liquid smelling of creosote, and leaving, after separation from empyreumatic oil, and evaporation, a black crystalline mass, which when sublimed, yields oxyphenic acid in thin colourless laminæ, and sometimes in rhombic prisms. From malabar kino (but not from butea-kino), a small quantity of oxyphenic acid may also be obtained by extraction with ether and evaporation,—or by precipitating the aqueous extract with acetate of lead, decomposing the lead precipitate with sulphuretted hydrogen, evaporating, and digesting the residue in ether (Eissfeldt).—4. Crude wood-vinegar evaporated to a syrup is shaken up with a saturated solution of common salt; the liquid separated from the tarry matter is agitated with ether; the ethereal liquid separated from the saline solution and the ether distilled off; and the residue (containing oxyphenic acid, acetic acid and tar-oil) distilled in a stream of carbonic anhydride, whereupon acetic acid passes over first, then oxyphenic acid and tar-oil, then a brown viscid oil. The middle portion of the distillate, which must be collected apart, solidifies on cooling in a reddish-yellow crystalline pulp, which, when pressed between bibulous paper and sublimed in a stream of carbonic anhydride, yields colourless oxyphenic acid. Or better: The wood-vinegar is shaken up with ether without previous evaporation; the residue obtained from the ethereal liquid by distilling off the ether is shaken up with a saturated solution of common salt; the saline solution, after separation from the oil, again shaken up with ether; the ether distilled off; and the residue also subjected to distillation: a liquid is then obtained, which, on cooling, yields tolerably pure crystals of oxyphenic acid. (Buchner.)

*Properties.*—Oxyphenic acid forms broad, white, strongly shining laminæ resembling benzoic acid, and rhombic prisms (Zwenger). Small shining rectangular prisms belonging to the trimetric system; bevelled with two faces resting on the acute lateral edges at an angle of 116° (Wagner and Neumann). It melts at 116°, and sublimes even at a lower temperature (Zwenger); melts, after drying, between 110° and 115°, and volatilises gradually at 130° (between 50° and 60° according to Wagner); melts at 111° or 112°; when perfectly dry, and volatilises even at ordinary temperatures (Eissfeldt); melts at 111°, and volatilises at the melting point, subliming in shining laminæ (Buchner). Boils between 240° and 245° (between 240° and 250°, according to Wagner), and yields colourless vapours which condense into a quickly crystallising oil (Wagner). The vapours have a pungent odour and excite coughing. It has a bitter taste and scarcely reddens litmus. Mixed with hydrochloric acid, it colours fir-wood violet, the colouring being stronger as the oxyphenic acid is more free from phenol. (Wagner.)

Oxyphenic acid dissolves readily in *water;* also in *oil of vitriol* and *hydrochloric acid*, very readily in *alcohol*, and very readily according to Zwenger, but with difficulty according to Buchner, in *ether*.

It quickly absorbs *ammoniacal gas*, and gives it off again in vacuo or at 100°. (Zwenger.)

Its aqueous solution forms, with *neutral acetate of lead*, a thick white precipitate, $C^6H^4Pb''O^2$, which is permanent in the air, nearly insoluble in water, but dissolves very readily in acetic acid. When dried in the cold, it appears greenish-white, but brownish when dried at 100°.

The aqueous solution of pyrocatechin does not colour *ferrous salts;* it colours *ferric salts* dark green and then forms a black precipitate; the dark green colour is changed by alkalis, even in very dilute solutions, to a beautiful violet-red like that of permanganate of potassium, and the green colour is restored by acids.

It does not precipitate *gelatin*, or the salts of *quinine*.

*Decompositions.*—1. Oxyphenic acid turns yellow when heated, and becomes somewhat richer in carbon. It also leaves a slight black residue when sublimed. This residue boiled with water, leaves an empyreumatic resin, and yields a brown decoction; on evaporating this liquid, a black film forms on the surface and a brown-black residue is left.—2. It burns with a bright flame.—3. Its aqueous solution turns reddish in contact with the *air*, and may be evaporated without decomposition.—4. It is rapidly decomposed by *chlorate of potassium* and *hydrochloric acid*, yielding perchloroquinone.—5. *Nitric acid* acts upon it with violence, evolving red vapours. The products of this reaction are oxalic acid and traces of a yellow nitro-acid, probably oxyphenic acid.—6.

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With aqueous *chloride of lime* or *acid chromate of potassium*, it forms a black liquid and a black precipitate.—7. With aqueous *caustic alkalis* or *alkaline carbonates* it forms a mixture which is yellow at first, then becomes greenish-yellow, and lastly black. The aqueous solution of oxyphenic acid produces a greenish precipitate with *silver solution*, the silver being partly reduced, and a dark brown precipitate with solution of *gold*. To *platinic* chloride it gradually imparts a green colour and then forms a greenish-brown precipitate. According to Wagner, it easily reduces *silver nitrate, auric chloride* and *platinic chloride;* and at a boiling heat, cupric *sulphate* or *acetate* mixed with potash; it also imparts a brown colour to cupric acetate, and then forms a black-brown precipitate. It is not altered by sulphurous acid. (Wagner.)

*Acetoxyphenic acid*, $C^6H^4(C^2H^3O)^2O^2$, is produced by the action of chloride of acetyl on oxyphenic acid. It is easily fusible, insoluble in water, but soluble in alcohol, whence it crystallises in needles. It does not even colour iron-salts. (Nachbaur, Ann. Ch. Pharm. cvii. 243.)

*Benzoxyphenic acid*, $C^6H^4(C^7H^5O)^2O^2$, is obtained in like manner as a viscid mass which solidifies in the crystalline state after a few days. It is insoluble in water, easily soluble in alkalis and in alcohol, and crystallises from the latter in funnel-shaped masses of rhombic crystals. The solution colours iron-salts green. (Nachbaur.)

**OXYPHENYL-SULPHURIC ACID.** $C^6H^6SO^4$.—This acid is formed, with evolution of nitrogen, when the aqueous solution of diazophenyl-sulphuric acid, $C^6H^4N^2SO^3$, is heated above 60°. Its silver-salt, $C^6H^5AgSO^4$, crystallises in small needles. (R. Schmitt, Ann. Ch. Pharm. cxii. 118.)

**OXYPEUCEDANIN.** See PEUCEDANIN.

**OXYPHORPHYRIC ACID.** A nitro-acid produced by the action of nitric acid on euxanthone (ii. 610).

**OXYPICRIC ACID.** $C^6H^3N^3O^8 = C^6H^3(NO^2)^3O^2$.—*Styphnic acid* (from στυφνός, astringent). *Artificial bitter* or *artificial tanin of Logwood-extract.*—This acid, which differs from picric or trinitrophenic acid by 1 at. oxygen, is produced by the prolonged action of nitric acid at the boiling heat on extract of logwood, euxanthone, gum-ammonium, asafœtida, galbanum, sagapenum, or the aqueous extract of fustic or sandal-wood. It was first obtained in an impure state by Chevreul in 1858 (Ann. Ch. lxvi. 116; lxxiii. 43), afterwards in the pure state and more exactly investigated by Erdmann in 1846 (J. pr. Chem. xxxvii. 409; xxxviii. 355), and a few weeks later by Böttger and Will (Ann. Ch. Pharm. lviii. 273).

*Preparation.*—1. *From Asafœtida.* 1 pt. of asafœtida in lumps of the size of a walnut is heated to a temperature between 70° and 75° in a wide porcelain basin, with 4 to 6 pts. nitric acid of specific gravity 1·2, free from sulphuric and hydrochloric acid; and, after the resin has become soft and divided, and a thick froth has risen,—which must be prevented from running over by stirring—the mass, which is then lemon-coloured and viscid, is kept, together with the surrounding nitric acid liquid, at the boiling heat, with frequent addition of fresh acid, till (in 5 or 6 hours) it is completely dissolved; after which the dark red-brown solution is evaporated nearly to a syrup and mixed with a small quantity of water. If it then gives a greasy resinous precipitate, it must be boiled for a longer time with nitric acid; but if it gives a yellowish sandy precipitate, it must be carefully evaporated to a thick syrup to drive off the greater part of the nitric acid; then heated to the boiling point with a tolerable large quantity of water; mixed with carbonate of potassium as long as effervescence ensues, but no longer (so as not to redissolve any undecomposed portion of the resin which rises to the surface when the liquid is neutralised); strained through grey paper; evaporated; and left to crystallise. The mother-liquor repeatedly evaporated and cooled yields an additional quantity of crystals of impure oxypicrate of potassium, till at last nitrate of potassium (but no oxalate) separates out. The needle-shaped crystals, united in red-brown crusts and nodules, are freed from the mother-liquor by draining on bibulous paper, twice recrystallised from water, with addition of animal charcoal, and dissolved in the smallest possible quantity of boiling water; nitric acid is then added; and the oxypicric acid, which separates after complete cooling as a yellowish-white powder, or in fern-like laminæ, is collected on a filter, washed several times with cold water, and after thorough drying, recrystallised from boiling absolute alcohol. This process yields 3 per cent. of oxypicric acid. (Böttger and Will.)

2. *From commercial extract of Logwood.*—The mode of preparation is similar to the preceding.

3. *From Euxanthone or Euxanthic acid.*—These substances are boiled for some time with nitric acid of specific gravity 1·31; the solution evaporated over the water-bath, below 100° towards the end; the sparingly soluble oxypicric acid separated from the oxalic acid by repeated crystallisation, and dissolved in dilute carbonate of ammonium; this solution saturated while warm with carbonate of ammonium, whereby the oxypicrate

of ammonium, which is insoluble in aqueous carbonate of ammonia, is made to crystallise in yellow four-sided prisms; these crystals, if too dark-coloured, are purified by animal charcoal; and the oxypicric acid is separated from them by hydrochloric acid.

4. *From Peucedanin.*—The oxypicric acid obtained by treating peucedanin with warm nitric acid, is mixed with potash to free it from the oxalic acid which is abundantly mixed with it; the oxypicrate of potassium which crystallises out is washed with cold water; its solution in hot water is precipitated by a lead-salt; and the acid separated from the precipitate. (Rothe, J. pr. Chem. xlvi. 376.)

*Properties.*—Oxypicric acid crystallises in pale yellow, regular, six-sided prisms resembling pyromorphite; they grate between the teeth, melt when carefully heated, and solidify in the radiated form on cooling. It has a slightly rough taste, neither bitter nor sour, but reddens litmus strongly, and when dissolved in alcohol, colours the skin permanently yellow. It dissolves, with yellow colour, in 104 pts. of water at 25° (Erdmann); in 88 pts. at 62° (Böttger and Will). It is easily soluble in *alcohol* and in *ether*; more easily in strong *acetic acid* than in water. It dissolves abundantly in strong *nitric acid*; less freely in strong *hydrochloric acid*, and is partially precipitated from both acids by water in the form of powder. It gives a copious precipitate with *gelatin*.

*Decompositions.*—1. Oxypicric acid heated somewhat above its melting point gives off inflammable vapours. When suddenly heated, it deflagrates like gunpowder, with a bright yellow flame, mostly bordered with orange-yellow, and leaves a residue of charcoal. When gradually heated, it gives off nitrous gas, nitrogen, carbonic anhydride, inflammable gas and water, and leaves very finely-divided charcoal; on red-hot iron it deflagrates with flame.—2. It is completely destroyed by boiling *nitrohydrochloric acid*, with formation of oxalic acid, whereas boiling concentrated nitric or hydrochloric acid alone has no action upon it.—3. It is decomposed by boiling *oil of vitriol*. It is not decomposed by boiling with excess of concentrated potash; and when digested with lime and ferrous sulphate, does not form a red liquid, as picric acid does, but a colourless liquid.—4. It is not altered by sulphydric acid, but the light yellow mixture of the acid dissolved in alcohol with *sulphide of ammonium*, immediately acquires a dark brown-red colour when heated, and leaves on evaporation a black mass, containing, besides sulphur and a small quantity of black powder, an ammonium-salt which may be dissolved out by water and whose acid resembles picric acid and oxypicric acid.—5. The hot aqueous acid dissolves *ferrous sulphide* with less evolution of sulphydric acid than might be expected. With *zinc* or *iron*, it likewise gives off a less than proportionate quantity of hydrogen, forming greenish-brown solutions. It does not act on cadmium, lead, copper or silver. Its powder strewn on *potassium* (not on sodium) takes fire when slightly pressed with a pestle.

OXYPICRATES.—Oxypicric acid easily decomposes carbonates. It is dibasic, forming neutral and acid salts. Nearly all oxypicrates detonate, when subjected to a gradually increasing heat (not by percussion), even more violently than the picrates. From the aqueous solutions of the heavy metallic salts of this acid, animal charcoal removes the whole of the oxide, especially from the styphnates of manganese, lead, nickel and copper salts. (Böttger and Will, Rothe.)

*Ammonium-salts.* α. *Neutral.* $C^6H(NH^4)^2(NO^2)^3O^2$.—The aqueous acid neutralised with ammonia and then saturated, while warm, with solid carbonate of ammonium, which diminishes the solubility of oxypicrate of ammonium in water, yields large orange-yellow needles which detonate slightly when heated and dissolve in water more readily than the acid salt (Böttger and Will). The crystals are monoclinic, exhibiting the combination $\infty P . [\infty P\infty] . \infty P\infty . [P\infty] . -P . +P . -P\infty$. Ratio of principal axis, clinodiagonal and orthodiagonal = 1 : 1·6609 : 2·090. Angle of inclined axes = 76° 52′. Angle $\infty P : \infty P$ in the clinodiagonal principal section = 104° 32′: $[P\infty] : [P\infty] = 130° 2′$. Cleavage imperfect parallel to $[\infty P\infty]$. (Schabus.)

β. *Acid.* $C^6H^2(NH^4)(NO^2)^3O^2$.—Obtained by neutralising one-half of the acid with carbonate of ammonium, adding the other half, then evaporating and cooling. A comparatively dilute solution yields large, light-yellow, flat needles, and a solution more concentrated by evaporation yields capillary interlaced needles, which detonate very slightly.

The *barium-salt*, $C^6HBa''(NO^2)^3O^2.2H^2O$, is very soluble, and crystallises in orange-coloured very shortened needles, which give off half their water at 100°.

The *cadmium-salt* is deliquescent.

The *calcium-salt*, $2C^6HCa''(NO^2)^3O^2.7H^2O$ ? is also very soluble, and crystallises in nodules which give off 10·22 per cent. (2 at.) water at 100°.

The *cobalt-salt* forms light-brown very soluble needles. The *ammonio-cobaltous salt* forms brown-yellow needles: the *potassio-cobaltous* salt, hard brown nodules.

The *cupric salt*, $C^6HCu''(NO^2)^3O^2.H^2O$, is obtained in light yellow needles by leaving a solution of cupric carbonate in oxypicric acid to evaporate. The *ammonio-*

*cupric salt* is obtained in brown, moderately soluble triclinic crystals, by dissolving cupric carbonate in a saturated solution of oxypicrate of ammonium. The *potassio-cupric salt*, $C^{12}H^{2}K^{2}Cu''(NO^{2})^{6}O^{4}.4H^{2}O$ ? prepared in like manner, forms tufts of brown needles which detonate with great violence when heated.

*Iron-salts.*—The filtrate obtained by precipitating the barium-salt with *ferrous sulphate*, slowly yields black-green crystals which dissolve readily and pass to a higher state of oxidation. The ammonium-salt mixed with iron alum forms yellow needles of *ferric oxypicrate.*

*Lead-salt.*—The *neutral salt* has not been obtained. A solution of neutral lead acetate mixed with oxypicric acid forms a light yellow flocculent precipitate consisting of a *basic salt*, $C^{12}H^{4}Pb''(NO^{2})^{6}O^{4}.2Pb''O.3H^{2}O$. It is insoluble in water, and when dry detonates by mere pressure.

The *magnesium-salt* is very soluble and difficult to crystallise.

The *manganese-salt* is obtained by precipitating the barium-salt with manganous sulphate, and evaporating in light yellow rhombic tablets, which when heated melt in their water of crystallisation and turn red. It gives off 22·98 per cent. water (10 at.) at 100°.

The *nickel-salt* crystallises with difficulty in light yellow, very soluble needles. The *nickel-potassium salt* forms brown crystalline crusts.

*Potassium-salts.*—The *neutral salt*, $C^{6}HK^{2}(NO^{2})^{3}O^{2}$, forms thin, truncated orange-yellow needles, sparingly soluble in water. Potash added in excess to the aqueous acid throws down this salt in the form of a crystalline powder. The *acid-salt*, $C^{6}H^{2}K(NO^{2})^{3}O^{2}.H^{2}O$, obtained by saturating half of a given quantity of oxypicric acid with carbonate of potassium, and then adding the other half, crystallises in light yellow capillary needles, which give off their water of crystallisation at 100°.

*Silver-salt*, $C^{6}HAg^{2}(NO^{2})^{3}O^{2}$. The solution of carbonate of silver in the aqueous acid at 60°, or the mixture of the potassium-salt with a moderately strong solution of nitrate of silver prepared at 60°, yields, when somewhat quickly cooled, light yellow, flat needles, three inches long, or by slow cooling, laminæ which dissolve sparingly in water, and from whose solution the silver is reduced on boiling, with decomposition of the acid.

*Sodium-salts.*—The *neutral salt*, $2C^{6}HNa^{2}(NO^{2})^{3}O^{2}.5H^{2}O$ (?), crystallises in small light yellow needles, very soluble in water, and giving off the whole of their crystallisation-water at 100°. The *acid-salt* has not been obtained in the crystalline state.

The *strontium-salt*, $C^{6}HSr''(NO^{2})^{3}O^{2}.2H^{2}O$, is much more soluble than the barium-salt, but crystallises very easily from a moderately concentrated solution in very large nodules composed of long light yellow needles, which give off 7·02 per cent. water at 100°.

**OXYPINITANNIC ACID.** $C^{14}H^{16}O^{9}$.—An acid said by Kawalier (Wien. Acad. Ber. xi. 354) to occur about Christmas in the needles of the Scotch fir (*Pinus sylvestris*). To extract it, the comminuted needles are exhausted with boiling alcohol of 40 per cent.; the alcohol is distilled off; and the residue is mixed with water, which throws down a green mass of resin, while the supernatant liquid retains in solution pinipicrin sugar, oxypinitannic acid, pinitannic acid and traces of citric acid. This liquid may be rendered filtrable by addition of a few drops of neutral lead-acetate; and on mixing the filtrate with an excess of that reagent, oxypinitannate of lead is precipitated. This precipitate is then to be digested with dilute acetic acid; the filtrate precipitated by basic lead-acetate, which throws down pure oxypinitannate of lead; the washed precipitate decomposed by sulphydric acid; and the filtrate evaporated over the water-bath.

Oxypinitannic acid is a brownish inodorous powder having a very astringent taste, easily soluble in *water*. The solution is coloured yellow by *ammonia;* forms with baryta-water a yellow liquid which deposits red flocks when heated; is coloured green by *ferric chloride;* and forms a greenish-brown precipitate with *cupric sulphate* and a small quantity of ammonia. It is not precipitated by tartar-emetic or nitrate of silver. When supersaturated with ammonia, it quickly absorbs oxygen from the air and acquires a brown colour. By boiling with *hydrochloric acid*, it acquires the colour of carmine. When boiled with dilute *sulphuric acid* it deposits a red powder, but does not yield sugar. The ammonium-salt mixed with *silver-nitrate*, becomes turbid and deposits metallic silver when heated.

**OXYPROTEIN.** See PROTEIN.

**OXYPYROLIC ACID.** $C^{7}H^{12}O^{5}$? (Arppe, Ann. Ch. Pharm. xcv. 242.)—An acid said to be produced simultaneously with succinic acid by the action of nitric acid on sebacic acid. It crystallises sometimes in colourless laminæ, sometimes in spherical masses; dissolves in 42 pts. of water at 20°, much more easily in boiling water, melts at 130°, and decomposes at higher temperatures. It gave by analysis 47·7 to 48·1 per cent. carbon, and 6·6 to 6·9 hydrogen, the above formula requiring 47·7 carbon and 6·8 hydrogen. The silver-salt gave 57·0 per cent. silver, the formula $C^7H^{10}Ag^2O^5$ requiring 55·4 per cent. According to Wirz (Ann. Ch. Pharm. civ. 257), this acid is identical with pimelic acid, $C^7H^{12}O^4$. Arppe in a later communication (Ann. Ch. Pharm. cxv. 143) states that the acid obtained as above easily passes from the granular into the laminar form, that the composition of granular acid agrees best with the formula of pimelic acid, but the laminar acid has the composition $C^7H^{12}O^5$.

**OXYQUININE.** A compound formed by boiling sulphate of quinine with nitrite of potassium. Nitrogen gas is then evolved, and the liquid when cold, yields with ammonia a white crystallo-granular precipitate, the alcoholic solution of which leaves on evaporation a transparent amorphous residue, quickly becoming crystalline in contact with water. The crystalline granules melt at 100° in their water of crystallisation, give it off at 130° and are converted into a colourless transparent mass, which remains solid at 140°, and contains $C^{20}H^{24}N^2O^3$ = quinine + 1 at. oxygen. It is insoluble in water, soluble in alcohol and ether, and less bitter than quinine. (Schützenberger, Compt. rend. xlvii. 81.)

**OXYRROPHONE** (from *ροφάνειν*, to absorb). A name applied by Döbereiner to platinum-black, because, according to his observations, it absorbs oxygen from the air and not nitrogen.

**OXYSALICYLIC ACID.** $C^7H^6O^4$. (Lautemann, Ann. Ch. Pharm. cxx. 299; Jahresb. 1862, p. 397.)—This acid, metameric with carbohydroquinonic (iii. 214), hypogallic and protocatechuic acids, is produced by boiling a solution of mono-iodosalicylic acid in caustic potash. When the reaction is completed (*i. e.* when a drop of the liquid mixed with hydrochloric acid no longer gives a precipitate of iodosalicylic acid) the liquid is to be slightly supersaturated with hydrochloric acid, and filtered when cold; and the filtrate shaken up with ether, which takes up nothing but oxysalicylic acid, and leaves it on evaporation as a brown crystalline mass. The acid is purified by treating its solution with acetate of lead and sulphydric acid.

Oxysalicylic acid forms highly lustrous needles easily soluble in *water*, *alcohol*, and *ether*. The aqueous solution mixed with *ferric chloride* acquires a deep blue colour, changing to a splendid violet on addition of acid carbonate of sodium. The crystallised acid contains no water of crystallisation; it melts at 193° and is resolved between 210° and 212° into carbonic anhydride and oxyphenic acid $C^6H^6O^2$, together with its isomer hydroquinone.

The salts of oxysalicylic acid are very unstable; those of the alkaline earth-metals turn brown and decompose when their aqueous solutions are exposed to the air. The acid, in contact with alkalis, instantly becomes reddish, and soon afterwards brown.

**Dioxysalicylic** or **Gallic Acid,** $C^7H^6O^5$, is produced in like manner by the action of boiling potash on di-iodosalicylic acid (ii. 760), but a considerable portion of the gallic acid thus formed is converted during the process into pyrogallic acid, the potash acting upon it under these circumstances in the same manner as a high temperature. Di-iodosalicylic acid heated for six hours to 150° in a sealed tube with excess of potassium carbonate, yields a mixture of salicylic, oxysalicylic, and dioxysalicylic acids.

**OXYSALTS.** Salts of oxygen-acids, or oxides in which the hydrogen of the type $nH^2O$ is replaced, partly by acid, partly by basylous radicles. (See SALTS.)

**OXYSTRYCHNINES.** (Schützenberger, Compt. rend. xlvii. 79.)—Compounds produced by the oxidation of strychnine. When sulphate of strychnine is boiled with nitrite of potassium in aqueous solution, nitrogen is abundantly evolved, and the liquid, on addition of ammonia, yields a light yellow flocculent substance which crystallises from alcohol in transparent orange-yellow crystals, apparently having the form of rhombic prisms with truncated edges, and consisting of oxystrychnine, $C^{21}H^{28}N^2O^6 = C^{21}H^{22}N^2O^2$ (strychnine) $+ 3H^2O + O$. The mother-liquor on further concentration deposits darker coloured orange-red prisms of dioxystrychnine, $C^{21}H^{28}N^2O^7 = C^{21}H^{22}N^2O^2 + 3H^2O + O^2$. Both compounds are insoluble in water and in ether, contain no water of crystallisation, decompose at 300°, and have a bitter taste, but not so strong as that of strychnine.

**OXYSULPHIDES.** Compounds of oxides and sulphides, or sulphides in which the sulphur is partly replaced by oxygen. Many metallic oxysulphides occur as natural minerals, *red antimony* or *kermesome* for example; many others are formed artificially, as *antimonial crocus* or *saffron* (i. 328).

**OXYSULPHOCARBONIC ETHERS.** See SULPHOCARBONIC ETHERS.

**OXYSULPHOPLATINOCYANIDE OF POTASSIUM.** See CYANIDES OF PLATINUM (ii. 267).

**OXYSULPHOSULPHUROUS ACID.** Syn. with HYPOSULPHUROUS ACID (see SULPHUR, OXYGEN-ACIDS OF).

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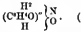
**OXYSYLVIC ACID.** $C^{20}H^{30}O^4$?—A viscid substance obtained by oxidation of sylvic acid (*q. v.*).



**OXYTEREPHTHALAMIC ACID.** $C^8H^7NO^3 = \left.\begin{matrix}H^2\\(C^8H^4O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (De La Rue and Müller, Proc. Roy. Soc. xi. 112; Jahresb. 1861, p. 425.)—Produced by the action of reducing agents on nitroterephthalic acid. It crystallises in thin prisms or moss-like aggregations of lemon-yellow colour. It is sparingly soluble in cold water, alcohol, ether and chloroform, and like its analogues, glycollamic acid, &c., unites both with bases and with acids.

The *oxyterephthalamates* are crystallisable and easily soluble in water and in alcohol, forming strongly fluorescent solutions; the compounds of oxyterephthalamic acid with *acids* are likewise crystallisable, but are decomposed by a large quantity of water; the acid solutions are not fluorescent.

The *ethers* of oxyterephthalamic acid are obtained by reduction of the nitroterephthalic ethers. The *methylic ether* is crystalline and soluble in warm alcohol; the *ethylic ether* forms large crystals resembling uranic nitrate, and forming a strongly fluorescent solution.

By the action of nitrous acid on oxyterephthalamic acid in alcoholic solution, a number of compounds are formed analogous to those which Griess obtained from oxybenzamic acid (p. 292).

**OXYTEREPHTHALIC ACID,** $C^8H^{12}O^8$, is produced, with copious evolution of nitrogen, by the action of nitrous acid on oxyterephthalamic acid. The *salts* are crystallisable, and less soluble than the corresponding terephthalates. The *neutral ethers* are liquid; so also is the *chloride of oxyterephthalyl*, which is easily soluble in water and in alcohol. (De La Rue and Müller.)

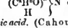
**OXYTOLIC ACID.** $C^7H^6O^3$. (Fittig, Ann. Ch. Pharm. cxx. 966.)—An acid, isomeric with salicylic and oxybenzoic acids, and perhaps also with ampelic acid (i. 201). It is produced by the oxidation of toluene (hydride of benzyl, i. 573). When toluene (boiling between 108° and 113°) is boiled for four or five days with a mixture of 1 pt. commercial nitric acid and 2 pts. water, a crystalline mixture of acids is obtained which are somewhat difficult to separate. On repeatedly treating the crystalline mass which remains after the distillation of the unaltered toluene and the nitrotoluene with a small quantity of hot water, so that about a fourth part shall remain undissolved, and leaving the solution to cool, oxytolic acid crystallises out, and may be purified by distillation, conversion into a calcium-salt, and repeated crystallisation of the latter, till the acid separated from it melts constantly at 180°.

The mother-liquor of the oxytolate of calcium yielded a calcium-salt, the acid of which appeared to be impure benzoic acid. The less soluble portion of the product of the oxidation above described contained an acid which exhibited nearly the composition $C^7H^6O^4$; but it did not melt at a constant temperature, and still contained nitrogen; whence Fittig concludes that it consisted of oxytolic acid contaminated with a nitro-compound.

Oxytolic acid is sparingly soluble in cold water, but dissolves more freely in hot water and in alcohol. It crystallises from water in colourless needles, melts at 180°, solidifies at 177°, sublimes below its melting point and distils undecomposed at higher temperatures. The vapour, both of the dry acid and of the aqueous solution, excites coughing, like benzoic acid.

Oxytolic acid is monobasic. The *potassium-salt*, $C^7H^5KO^3$, is very soluble in water, and crystallises from alcohol in small needles. The *sodium-salt* is precipitated as a jelly from its aqueous solution by alcohol. The *barium-salt*, $C^{14}H^{10}Ba''O^6$, gives off its water of crystallisation (amount not determined) over oil of vitriol. The *calcium-salt*, $C^{14}H^{10}Ca''O^6.3H^2O$, crystallises in needles soluble in water and in alcohol. The *silver-salt*, $C^7H^5AgO^3$, is a white precipitate which dissolves in hot water, and crystallises therefrom in needles. *Iron*, *copper*, and *lead-salts* are likewise obtained by precipitation with oxytolate of ammonium.

The reactions of oxytolic acid resemble those of Laurent's ampelic acid more than those of either of its other isomers (i. 201).



**OXYTOLUAMIC ACID.** $C^8H^9NO^2 = \left.\begin{matrix}H^2\\(C^8H^6O)''\\H\end{matrix}\right\}N$ or *Amidotoluic acid*, $C^8H^7(NH^2)O^2$; also, but improperly, called *Toluamic acid*. (Cahours, Ann. Ch. Pharm. cvii. 147.)—Obtained by reduction of nitrotoluic acid with sulphide of ammonium, just as its homologue, oxybenzamic acid (p. 290), is obtained from nitrobenzoic acid. It unites with acids, forming crystallisable compounds resembling those of oxybenzamic acid.

The *hydrochlorate*, $C^8H^9NO^3.HCl$, crystallises in small nacreous needles; the *chloroplatinate*, $(C^8H^9NO^3)^2.H^2Cl^2.Pt^{iv}Cl^4$, in red-brown needles.

*Diazotoluyl-oxytoluamic acid*, $C^{16}H^{14}N^2O^4 . \frac{3}{2}H^2O = C^8H^6N^2O^2.C^8H^9NO^3 . \frac{3}{2}H^2O$, is prepared by heating oxytoluamic acid with nitrous ether to 30°, just as the corresponding benzoic compound is obtained from oxybenzamic acid (p. 292). It forms yellow microscopic prisms, insoluble in water, alcohol, and ether; acids dissolve and decompose it; alkalis dissolve it unaltered. Its reactions are precisely analogous to those of diazobenzo-oxybenzamic acid.

The *potassium-*, *sodium-*, and *ammonium-salts* of this acid form easily soluble crystalline masses; the latter easily decomposes when its aqueous solution is boiled. The *barium-salt* is a yellowish precipitate, insoluble in water and in alcohol. The *silver-salt* is a white gelatinous precipitate. (Griess, Ann. Ch. Pharm. cxvii. 59.)

**OYSTERS.** The body of the oyster consists mainly, according to Mulder, of an albuminoïdal or protein substance, which coagulates at 90°, and is then soluble in strong acetic acid. Oysters contain 0·5 per cent. of salts.

Dried oyster-shells contain, according to Buchholz and Brandes, 9·8 per cent. calcic carbonate, 1·2 calcic phosphate, 0·5 albuminous substance, and 0·2 alumina (?). According to a more recent investigation by Schlossberger (Ann. Ch. Pharm. xcviii. 99), oyster-shells consist of three anatomically distinct layers: 1. An inner layer, the so-called mother-of pearl, smooth, shining, and semi-transparent: Carpenter's *subnacreous substance*.*—2. The brown, hard scales, forming the outer edges of the successive laminæ of which the upper shell is composed, these laminæ being placed one over the other, like tiles on a roof; Carpenter's *prismatic cellular substance.*—3. A white, dull, opaque, friable substance, called by Schlossberger the *chalky layer*, interposed here and there between the laminæ of the shell. These three layers were found to contain:

| | 1 | | 2 | 3 |
|---|---|---|---|---|
| Carbonate of calcium . . . . . | 94·7 | 98·3 | 89·1 | 88·6 |
| Organic matter . . . . . . | 2·2 | 0·8 | 6·3 | 4·7 |
| Other salts (and loss) . . . . . | 3·1 | 0·8 | 4·6 | 6·7 |

The salts contain small quantities of phosphoric acid and alkalis, with traces of silica and sulphuric acid.

The organic substance which remains on treating the shells with dilute sulphuric acid consists mainly of brown films, which are insoluble in hot water, even under increased pressure, dissolve gradually with aid of heat, in concentrated mineral acids, but only partially in potash-ley of 50 per cent. The portion insoluble in potash contains 50·7 per cent. carbon, 6·5 hydrogen, and 16·7 nitrogen, and is therefore similar in composition to Frémy's conchiolin (i. 1107), and is distinguished from chitin (i. 874) by its large amount of nitrogen. (Schlossberger.)

*Oyster water.* The water within the shell of the oyster is not simply sea-water, but is distinguished from it by containing less salts and more organic matter. When shaken up with ether, it deposits an albuminous substance containing 8·75 per cent. nitrogen. This albuminous matter amounts to 0·00056 of the liquid, which is composed of 95·888 pts. water, 3·022 salts, 0·560 azotised matter, 0·529 non-azotised matter = 100). The weight of liquid in the oyster is nearly equal to that of the flesh; it probably contributes to alimentation. A dozen oysters weighing 1·482 were found to be composed of 1·209 shell, 0·112 flesh, and 0·102 liquid. On calculating the quantity of alimentary matter equivalent to the nitrogen, it is found that a dozen oysters contain a quantity of azotised matter equal to about one-tenth of the ration (? daily) of a man. (Payen, Bull. Soc. Chim. ii. 235.)

**OZARKITE.** An amorphous or fibrous variety of Thomsonite from the Ozark mountains, Arkansas, where it occurs with elæolite; often also mixed with apatite (see Thomsonite).

**OZOCERITE** or **OZOKERITE.** A fossil resin discovered by Meyer in a sandtone in Moldavia, in the vicinity of coal and rock-salt. It also occurs at Gresten near Gaming in Austria, and at [illegible]ruskawicsz in Galicia; also at the Urpeth colliery, Newcastle-on-Tyne. It is like a resinous wax in consistence and translucency, sometimes with a foliated structure. Its colour is brown or brownish-yellow by transmitted light; leek-green by reflected light. Odour pleasantly aromatic. Specific gravity = 0·94—0·97. Melts at 62° (Schrötter), at 84° according to Malaguti; boils at 210° (Schrötter), at 300° (Malaguti). According to Johnston, the Urpeth variety melts at 60° and boils at 121°. It distils without decomposition, is not altered by strong acids, and very little by hot concentrated alcohol. The Moldavian variety dissolves but slightly in ether, whereas the Urpeth variety dissolves in ether to the amount of four-fifths, and separates on evaporation in brown flocks which melt at 38·9° to a yellowish-brown liquid. Three or four substances are supposed to be here included. The composition of ozocerite is as follows:

---

* Cyclopædia of Anatomy, art. Shell.

| | Moldavia. | | Urpeth. |
|---|---|---|---|
| | Malaguti. | Schrötter. | Johnston. |
| Carbon | 85·75 | 86·20 | 86·80 |
| Hydrogen | 15·15 | 13·79 | 14·06 |
| | 100·90 | 99·99 | 100·86 |

It is decomposed by dry distillation, yielding, according to Malguti, 10·34 per cent. gas, 74·01 oily matter, 12·55 crystalline substance, and 3·10 carbonaceous residue. (Gerh. iv. 399. Dana, ii. 474.)

Bertolio (Jahresb. 1860, p. 797) examined a fossil resin sent from Rio Janeiro as ozocerite, but of unknown origin. It was yellow, shining, greasy to the touch, of the hardness of talc, with a conchoïdal fracture. Specific gravity 0·98. It melted at 85°, and boiled at 245°, turning brown and emitting a fatty odour. It dissolved in hot alcohol and separated on cooling as a white powder composed of laminæ. Gave by analysis 69·5 to 70·2 per cent. carbon and 12·2 hydrogen, approximating to the composition of monomargarin or monostearin.

**OZONE.** See OXYGEN (p. 299).

**OZONE-HYDROGEN.** According to Osann, hydrogen evolved by electrolysis from water acidulated with sulphuric acid, possesses stronger reducing properties than ordinary hydrogen, inasmuch as a piece of coke or spongy platinum immersed in the gas thus obtained, or used as the negative pole in the circuit in which the acidulated water is decomposed, acquires the power of reducing silver from a solution of the sulphate, and of producing a blue colour in a solution of ferric chloride mixed with ferricyanide of potassium: hence he calls it ozone-hydrogen. According to later experiments, however, it appears that to obtain this active hydrogen it is necessary to use a recently prepared mixture of water and fuming sulphuric acid. (See Jahresb. 1853, p. 316; 1854, p. 286; 1855, p. 292; 1856, p. 273; 1857, p. 81; 1858, p. 64.)

**OZONE-WATER.** An aqueous solution of ozone, which, according to Meissner (Jahresb. 1862, p. 130), exhibits in certain cases an action opposed to that of peroxide of hydrogen, preventing the separation of iodine from iodide of potassium by peroxide of hydrogen and dilute acids, or by nitrate or iodate of potassium with acids. When this solution is shaken up with peroxide of barium, a violent evolution of oxygen takes place, and the filtrate no longer exhibits the reactions of ozone. Meissner regards ozone-water as water combined with negative oxygen or ozone; peroxide of hydrogen as water combined with positive oxygen or antozone.

# P.

**PACHNELO.** The bark of the Pachnelo tree of Bogota contains berberine. (Perrins.)

**PACHNOLITE** (from πάχνη, rime). (A. Knop, Ann. Ch. Pharm. cxxvii. 61. —G. v. Rath, Pogg. Ann. cxix. 261.)—A fluoride of aluminium, calcium and sodium, occurring in Greenland cryolite as an efflorescence of small, shining, colourless transparent crystals lining the cavities of the cryolite, or in larger crystals of rectangular parallelopipedal form on the surface. The smaller crystals are rhombic combinations $\infty P \,.\, P \,.\, oP$ (Knop), also with the face $\frac{3}{2}P$ (v. Rath). The inclinations of the faces are as follows:

| | v. Rath. | Knop. |
|---|---|---|
| $\infty P : \infty P$ | 81° 28′ | 81° 24′ |
| $P : \infty P$ | 156° 0′ | 154° 10′ |
| $P : P$ in the macrodiagonal terminal edge | 92° 23′ | 93° 58′ |
| „ in the brachydiagonal terminal edge | 106° 49′ | 108° 8′ |
| „ in the basal edge | 132° 0′ | 128° 20′ |
| $\frac{3}{2}P : \frac{3}{2}P$ in the macrodiagonal-terminal edge | 86° 50′ | |
| „ „ in the brachydiagonal terminal edge | 102° 23′ | |
| „ „ in the basal edge | 147° 20′ | |

According to Knop's measurements, the ratio of the axes $a : b : c$ is 0·8601 : 1 : 1·3469.

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The mineral when slowly heated gives off aqueous vapour without acid reaction; but when quickly heated, it emits white acid vapours which condense on the sides of the glass tube and can no longer be volatilised; the residue melts easily to a translucent enamel. The sublimate is insoluble in water, but dissolves easily in hydrochloric acid, giving the reactions of alumina. The mineral dissolves easily in sulphuric acid with evolution of hydrofluoric acid.

It gave by analysis:

| Al | Na | Ca | F | $H^2O$ | | |
|---|---|---|---|---|---|---|
| 13·14 | 12·16 | 17·25 | 50·79 | 9·60 | = 102·94 | (Knop). |
| 13·20 | 12·06 | 18·05 | undet. | 9·36 | (v. Rath). | |

From these numbers Knop deduces the formula $3\left\{\begin{matrix}\frac{3}{5}\,Ca''\\ \frac{2}{5}\,Na^2\end{matrix}\right\}F^2.2Al'''F^3.2H^2O$, which is that of a hydrated cryolite having $\frac{3}{5}$ of the sodium replaced by calcium; this formula requires 12·29 per cent. Al, 12·38 Na, 17·25 Ca, 51·12 F, and 8·07 $H^2O$. v. Rath gives a formula in which two-thirds of the sodium of cryolite is replaced by calcium, and half the fluoride of aluminium by alumina; but he did not determine the fluorine.

**PACKFONG** or **PACKTONG.** Chinese nickel-silver (see COPPER, ALLOYS OF, ii. 51).

**PÆONIN.** A red colouring matter obtained from phenylic alcohol by the action of sulphuric and oxalic acids. Kolbe and Schmitt (Ann. Ch. Pharm. cxix. 169), by heating 1½ pt. phenylic alcohol (coal-tar creosote) with 1 pt. oxalic and 2 pts. strong sulphuric acid to 140°—150°, for four or five hours, obtained a dark brown-red mass, which after being freed from phenyl-sulphuric acid by boiling with water, solidified to a brittle resinous substance. This substance dissolves with splendid purple-red colour in ammonia and potash-ley, and separates on neutralisation in orange-coloured flocks, having when dry a splendid orange-red colour, like that of precipitated alizarin. It melts at 80°, and then gives off phenylic alcohol; loses its colour when treated with sodium-amalgam or with iron-filings and acetic acid, but is stable in combination with alkalis. It gives by analysis numbers agreeing with the formula $C^5H^4O$, and is regarded by Kolbe and Schmitt as probably related to rosolic acid.

Guinon, Marnas and Bonnet (Rép. Chim. app. iv. 450) prepare this red resinous colouring matter (which they designate as *péonine instable*) by heating 10 pts. phenylic alcohol with 4 to 8 pts. oxalic acid and 3 to 6 pts. sulphuric acid, and boiling with water as above; then heat it with 2½ pts. aqueous ammonia to 150° in a closed metallic vessel for three hours; and from the resulting solution, by a process not further described, they obtain the colouring matter in a form in which it withstands the action of acids (*péonine stable*). By heating 5 pts. of this product with 6 to 8 pts. of aniline for several hours, they further obtain a blue colouring matter (*azulin*), insoluble in water, but soluble in alcohol and in ether.

**PAGODITE.** Syn. with AGALMATOLITE.

**PAISBERGITE.** Syn. with RHODONITE.

**PAKOE KIDANG.** Syn. with CIBOTIUM CUMINGII (i. 962).

**PALÆO-CRYSTALS.** A term applied by Haidinger to the original minerals from which paramorphs or pseudomorphs are formed: thus augite which has been altered to steatite, serpentine, &c., is called palæo-augite, the mineral resulting from the alteration being the pseudomorph.

**PALAGONITE.** An amorphous mineral which, according to Bunsen and Sartorius v. Waltershausen, is an essential constituent of the volcanic formations of Iceland and Sicily. It has generally a brown or yellow colour and a vitreous or greasy lustre; hardness = 4 to 5; specific gravity = 2·4 to 2·7. It gives off water when heated, melts easily before the blowpipe to a black magnetic lead, and is easily decomposed and gelatinised by hydrochloric acid. It is however always mixed with a number of minerals, chiefly augite and felspar, which are not acted upon by acids; in the following analyses these foreign minerals are deducted. The analyses of Sicilian palagonite are by v. Waltershausen (*Vulkanische Gesteine*, p. 179); those of the Icelandic mineral are by Bunsen (Ann. Ch. Pharm. lxi. 265).

*a.* From Val di Noto, Palagonia.—*b.* Black palagonite tufa from Militello.—*c.* From Aci Castello.—*d.* From Trollkonugil on Hekla.—*e.* From Krisuvik.—*f.* From Sudafell: palagonite tufa.—*g.* From the Galepagos islands: rock forming a crater (Bunsen).—*h.* From Hof Beselich near Limburg (F. Sandberger, J. pr. Chem. xlvii. 463).—*i.* Black mineral analogous in composition to palagonite, from Honnef in the Siebengebirge (Wackernagel, *Rammelsberg's Mineralchemie*, p. 868).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
|---|---|---|---|---|---|---|---|---|---|
| Silica . . | 38·69 | 41·37 | 36·97 | 40·74 | 40·30 | 41·46 | 36·95 | 48·96 | 41·63 |
| Alumina . | 13·61 | 11·32 | 7·80 | 8·42 | 14·45 | 10·90 | 11·56 | 9·94 | 18·72 |
| Ferric oxide. | 14·51 | 15·54 | 21·01 | 18·00 | 14·60 | 18·12 | 10·71 | 10·54 | 2·36 |
| Ferrous oxide | . . | 1·80 | . . | . . | . . | . . | . . | . . | 7·83 |
| Lime . . | 8·38 | 9·03 | 5·31 | 8·75 | 6·88 | 8·55 | 7·95 | 4·98 | 1·07 |
| Magnesia . | 6·13 | 7·14 | 4·83 | 4·54 | 7·57 | 4·80 | 6·27 | 3·04 | 5·23 |
| Soda . . | 1·07 | 1·01 | 7·23 | 0·62 | 1·82 | 0·64 | 0·55 | 1 04 | 2·51† |
| Potash . | 1·35 | 1·10 | 0·94 | 0·43 | 0·44 | 0·40 | 0·77 | 0·82 | . . |
| Water . | 16·26 | 11·69 | 15·91 | 18·50 | 13·50 | 14·49* | 25·24 | 20·68 | 20·71 |
| Phosphoric anhydride | | . . | . . | . . | 0·44 | | | | |
| | 100 | 100 | 100 | 100 | 100 | 99·36 | 100 | 100 | 100·06 |

These analytical results cannot be included under any general formula; they show indeed that palagonite is either a mixture or a compound contaminated with foreign substances. Bunsen has suggested for the greater number of palagonites the formula $3(M^2O.SiO^2).Al^2O^3.3SiO^2.10H^2O$, which however does not agree exactly with any individual analysis.

**PALIGORSKITE.** A white asbestiform silicate of specific gravity 2·217 in the Paligorian mining district of the Ural. Contains, according to Scaftschenkow, 52·18 per cent. silica, 18·32 alumina, 8·19 magnesia, 0·59 lime, 12·04 combined water, and 8·46 water given off at 100° (= 99·84).

**PALISANDER WOOD.** A red dye-wood from Madagascar, the colouring matter of which is affected by the air and by solvents, in the same manner as that of sandal-wood, but has less of an orange tint and is less able to resist the action of alkalis than the latter, being changed thereby to green, olive-green and brown. (Arnaudon, Cimento, viii. 278.)

**PALLADAMINE.**
**PALLAD-DIAMINE.** } See PALLADIUM-BASES, AMMONIACAL.

**PALLADANILAMINE.**
**PALLADETHYLAMINE.** } See PALLADIUM-BASES, ORGANIC.

**PALLADIUM.** *Atomic weight* 126. *Symbol* Pd.—A metal of the platinum group, discovered by Wollaston in 1803 (Phil. Trans. 1804, p. 419). The oxide and many of the other compounds were discovered and investigated by Berzelius (Pogg. Ann. xiii. 454).

*Occurrence.*—1. Single grains of pure palladium, sometimes of octahedral form, are mixed with the grains of platinum from Brazil. Native palladium mixed with gold and selenide of lead is also found at Tilkerode in the Hartz.—2. Palladium occurs in the platinum ore of South America (amounting to 1 pt. in 200 of the Peruvian ore), from St. Domingo, and from the Ural.—3. It occurs, alloyed with gold, in an auriferous sand from Zacotinga and Condonga in Brazil, mixed with specular iron ore: the palladium in this ore amounts to 5 or 6 per cent. Also alloyed with gold and silver in the *Oro pudre* of Porpez in South America: this mineral contains 10 per cent. of palladium.

*Extraction.* 1. From *platinum ore.*—The ore is digested in nitromuriatic acid; the acid solution decanted from the insoluble residue is neutralised; the platinum is precipitated by sal-ammoniac; and the palladium is thrown down from the filtrate by cyanide of mercury as a white flocculent cyanide which yields metallic palladium by calcination. (See further *Gmelin's Handbook*, vi. 256, 257, 261, 264, 267.)

2. From the *palladiferous gold* of Brazil. The gold-dust is fused with an equal weight of silver and a certain quantity of nitre, whereby the earthy matters and the greater part of the base metals are removed in the form of slag; the alloy is then cast in the form of bars; the latter again fused in a black lead crucible, stirring constantly with an equal weight of silver, so that the gold amounts to about one-fourth of the whole mixture. The alloy is then very finely granulated by pouring it through an iron sieve into water; the granules are heated in a porcelain basin with an equal quantity of nitric acid and an equal quantity of water, as long as any action goes on; the liquid is decanted; and the residual gold is boiled for two hours with a quantity of pure nitric acid equal to two-thirds of the granules used, after which it is washed with hot water, dried, and fused into a button. From the resulting nitric acid solutions, the silver is precipitated by common salt. The remaining liquid being transferred to wooden vessels, the palladium and copper are precipitated by zinc; the black powder is dissolved in nitric acid; the solution supersaturated with ammonia, which generally leaves undissolved a small quantity of platinum, iron, and lead; and the filtrate containing the palladium and copper is very slightly supersaturated with hydrochloric acid, whereby the greater

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[*] And $CO^2$.

[†] Manganous oxide.

part of the palladium is precipitated in the form of yellow ammonio-protochloride, which is then washed with cold water and converted into pure palladium by ignition. The remainder of the palladium and the whole of the copper may be precipitated from the hydrochloric acid solution by iron. (Johnson, J. pr. Chem. xi. 309.—Cock, Phil. Mag. [3] xxiii. 16; also Ann. Ch. Pharm. xlix. 236.)

*Properties.*—Palladium is a white metal intermediate in colour and lustre between silver and platinum. As obtained by ignition from the cyanide or from chloride of palladium and ammonium, it forms a grey spongy mass. Finely divided palladium floating on water appears blood-red by transmitted light. Native palladium occurs in six-sided tables, with distinct cleavage parallel to the terminal faces; white, with a strong lustre, of almost microscopic size, and attached to laminæ of native gold (G. Rose); also in minute octahedrons (Haidinger). The native palladium from Brazil exhibits a fibrous structure, and may be thereby distinguished and separated from the grains of platinum with which it is mixed (Wollaston). Specific gravity of fused palladium, 11·04 at 18° (Cloud), 11·3 (Cock), from 11·3 to 11·8 (Wollaston), 11·4 at 22·5° (Deville and Debray); of hammered palladium, 11·8 (Cock), 11·852 (Lampadius), rather more than 12·0 (Vauquelin), 12·148 (Lowry). Palladium is about as hard as platinum; ductile, but somewhat less so than platinum; and may be rolled out into thin leaves. It is the most fusible of all the metals of the platinum group, beginning to fuse at the strongest heat of a forge-fire, and melting perfectly before the oxyhydrogen blowpipe. When heated on lime in Deville's furnace (p. 313) to the melting point of iridium, it volatilises in green vapours which condense to a bistre-coloured dust of metal and oxide. It oxidises at a lower temperature than silver, and is always covered on the surface with a thin film of oxide. If it be freed from this coating by ignition in a reducing flame, and held while still hot in a stream of mixed air and combustible gas, it continues to glow like platinum. If exposed to the air in the melted state it absorbs oxygen and spits like silver; but the absorbed gas is not given off till just as the metal begins to solidify, so that the mass, though very dense on the surface, remains porous within. (Deville and Debray.)

Palladium is very slightly attacked by concentrated *hydrochloric* or *sulphuric acid*, even at the boiling heat. It dissolves in *nitric acid* without evolution of gas, but communicates a brownish-red colour to the liquid, from formation of nitrous acid. It dissolves with facility in *nitromuriatic acid*. Its surface is blackened by tincture of *iodine*, which has no effect on platinum.

Palladium is sometimes used for making the divided scales of astronomical instruments, for which it is well adapted, being light, nearly as white as silver, and not blackened by sulphurous emanations. It is also used for making the smaller divisions of the grain or gramme.

Palladium in most of its compounds is diatomic, as in the di-chloride $Pd''Cl^2$, the di-iodide $Pd''I^2$, the protoxide $Pd''O$, &c. A tetrachloride occurs in certain double salts, and the dioxide $Pd^{iv}O^2$ is known in combination with water.

**PALLADIUM, ALLOYS OF.** Palladium unites with most metals, but only a few of its alloys are of any practical importance. With antimony and arsenic it forms brittle alloys, the combination in each case being attended with ignition. (Fischer.)

Barium unites with it at the heat of the oxyhydrogen blowpipe, forming a silver-white alloy which gradually oxidises on the surface. (Clarke.)

Equal parts of bismuth and palladium form a grey alloy having the hardness of steel. (Chenevix.)

Copper and palladium unite without incandescence; 4 pts. copper and 1 pt. palladium form a white ductile alloy; equal weights of the two metals yield a yellow-brown brittle alloy, harder than wrought iron, and when fused together before the oxyhydrogen blowpipe, an easily fusible alloy of pale colour, susceptible of a high polish, easily attacked by the file (Clarke). Palladium forms with copper an alloy similar in properties and composition to that which it forms with tin (*vid. inf.*), and obtained in a similar manner. (Deville and Debray).

With gold, palladium forms several alloys, the combination always taking place without ignition. 1 pt. palladium and 1 pt. gold form a grey alloy having the colour of wrought iron, less ductile than either of the component metals, and of coarse-grained fracture; 1 pt. palladium and 4 pts. gold yield a white, hard, ductile alloy; an alloy of 1 pt. palladium and 6 pts. gold is almost white. The native alloy of palladium, gold and silver from Porpez contains 85·98 per cent. gold, 9·85 palladium, and 4·17 silver. (Berzelius.)

The alloy of palladium and iron is very brittle; but an alloy of 1 pt. palladium and 100 pts. steel is well adapted for cutting instruments which require to be perfectly smooth on the edge. (Faraday and Stodart.)

With **lead**, palladium forms a grey, hard, brittle alloy, having a fine-grained fracture, and of specific gravity 12·0. The combustion is attended with ignition.

Respecting the **mercury-compounds** of palladium, see iii. 888.

**Nickel** and palladium unite at the heat of the oxyhydrogen blowpipe, forming a highly lustrous, very malleable alloy. (Clarke.)

Equal parts of **platinum** and palladium unite at a temperature somewhat above the melting point of the latter, forming a grey alloy of specific gravity 15·141, as hard as wrought iron, less ductile than the gold alloy. (Chenevix.)

An alloy of 1 pt. **silver** and 9 pts. palladium is used by dentists.

An alloy of equal pts. palladium and **tin** is somewhat softer than wrought iron, and has a fine-grained texture (Chenevix). When palladium is fused at a red heat with six times its weight of tin, and the resulting mass is treated with hydrochloric acid, there remains an alloy having the composition $Pd^3Sn^2$, crystallised in slender shining laminæ. Similar alloys of palladium with silver and with copper are obtained in like manner. (Deville and Debray).

Palladium dissolves in melted **zinc**, but does not unite with it in definite proportions; on treating the resulting alloy with hydrochloric acid, pure palladium remains undissolved. (Deville and Debray.)

**PALLADIUM, BROMIDE OF.** Palladium dissolved in a mixture of nitric and hydrobromic acids, yields on evaporation a chestnut-brown mass insoluble in water, but soluble in aqueous hydrobromic acid, and forming dark brown double salts with the bromides of potassium, manganese and zinc. (Bonsdorff, Pogg. Ann. xix. 347.)

**PALLADIUM, CARBIDE OF.** Palladium fused in a crucible filled with lampblack becomes so brittle, that if struck with a hammer while red-hot, it falls to powder and gives off a white fume. Respecting the formation of palladium-carbide in an alcohol-flame, see below.

**PALLADIUM, CHLORIDES OF.** The *dichloride* or *Palladious chloride*, $Pd''Cl^2$, is prepared by dissolving palladium in hydrochloric acid to which a little nitric acid is added, and evaporating the solution to dryness, to expel the excess of acid. The compound is a mass of a dark brown colour, which becomes black when made anhydrous by heat, and may be fused in a glass vessel. When heated in platinum vessels, it becomes contaminated with the chloride of that metal. When dissolved with *chloride of potassium*, it forms a double salt, $K^2Pd''Cl^4$, which is soluble in cold, and considerably more so in hot water, and crystallises in four-sided prisms of a dull yellow colour. Dichloride of palladium also forms double salts with the chlorides of ammonium, sodium, and several other metals.

The *tetrachloride* or *Palladic chloride*, $Pd^{iv}Cl^4$, is obtained in solution when the dichloride is dissolved in concentrated nitromuriatic acid, and the solution is only slightly heated. Its solution is of so dark a colour as to appear black, and gives a red precipitate with chloride of potassium. When the solution is diluted or heated, chlorine gas is evolved, and dichloride of palladium reproduced. The double salt of this chloride and chloride of potassium is obtained by treating potassio-palladious chloride in fine powder with nitromuriatic acid, and evaporating the supernatant liquid to dryness. It forms a cinnabar-red powder, in which octahedral crystals can be perceived, both the palladic and palladious double chlorides being isomorphous with the corresponding compounds of platinum. When treated with hot water, this double salt emits chlorine, and is in a great measure decomposed.

**PALLADIUM, CYANIDES OF.** Palladium forms two cyanides analogous to the chlorides (see CYANIDES, ii. 260).

**PALLADIUM, DETECTION AND ESTIMATION OF.** 1. *Reactions.*—Nearly all palladium-compounds are decomposed by heat, leaving metallic palladium: which may be distinguished from platinum by its solubility in nitric acid, by its reaction with tincture of iodine (p. 328), or by its behaviour in an alcohol-flame. If held in the inner flame of a spirit-lamp, it unites with carbon, without first being heated to redness; and if then quickly removed from the flame, it glows vividly in the air till all the carbon is burnt away and pure palladium is left: this reaction is exhibited most conspicuously by finely-divided palladium which has been closely compressed: spongy platinum does not exhibit it at all.

*Palladious salts* are for the most part brown or red; their taste is astringent, but not metallic. The metal is precipitated from the solutions of palladious salts by *phosphorus*, by *sulphurous acid*, by *nitrite of potassium*, by all the *metals* which reduce silver, by *formate of potassium*, and by *alcohol* at a boiling heat. *Sulphydric acid* and *sulphide of ammonium* throw down the brown sulphide of palladium, insoluble in the latter reagent. *Hydriodic acid* and *iodide of potassium* throw down a black precipitate of iodide of palladium, visible even to the 500,000th degree of dilution. This reaction serves for the separation of iodine from bromine: for alkaline bromides do not

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precipitate palladious salts. *Potash* or *soda* forms a brown precipitate of a basic salt, soluble, with the aid of heat, in excess of the reagent. *Ammonia* produces no precipitate in a solution of palladious nitrate; but from a solution of the chloride, it throws down a flesh-coloured precipitate of ammonio-chloride of palladium, soluble in excess of ammonia. The *carbonates of potassium* and *sodium* form a brown precipitate of hydrated palladious oxide. *Carbonate of ammonium* acts like ammonia. *Phosphate of sodium* forms a brown precipitate. *Ferrocyanide* and *ferricyanide of potassium* form no precipitate, but the liquid after a while coagulates into a jelly. *Cyanide of mercury* throws down a white precipitate of cyanide of palladium. *Stannous chloride* forms a black precipitate which dissolves with intense green colour in hydrochloric acid. *Ferrous sulphate* precipitates palladium slowly from the nitrate, but not from the chloride. The reactions of palladium with sulphydric acid, cyanide of mercury, and iodide of potassium taken together, serve to distinguish it from all other metals.

*Palladic salts* are very unstable, being easily reduced to palladious salts by heat, and by reducing agents: hence their reactions are scarcely known. The dark brown solution of the tetrachloride is easily distinguished from the similarly coloured solutions of tetrachloride of platinum or iridium by its property of giving off chlorine when heated and leaving the dichloride.

*Estimation and Separation of Palladium.*—Palladium is always estimated in the metallic state. It is precipitated from its solutions in the form of cyanide by a solution of cyanide of mercury, the liquid not containing any excess of acid. The precipitated cyanide is then reduced to the metallic state by calcination.

Palladium may be separated from nearly all other metals, either by precipitation with cyanide of mercury or with sulphydric acid, or by the solubility of its oxide in ammonia. If however the solution contains alcohol, gold, platinum and some other metals may be precipitated at the same time. Palladium cannot be separated from platinum by nitric acid: for an alloy of palladium with a small quantity of platinum is completely dissolved by that acid.

To separate palladium from copper, with which it is associated in platinum-ore, the two metals are precipitated together by sulphydric acid, and the precipitate, while still moist, is roasted, together with the platinum, as long as sulphurous anhydride continues to escape. The metals are thereby converted into basic sulphates, which must be dissolved in hydrochloric acid, and the solution mixed with nitric acid and chloride of potassium, and evaporated to dryness. A dark saline mass is thus obtained, consisting of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium; and on treating this mass with alcohol of specific gravity 0·833, the two former salts are dissolved and the double chloride of palladium and potassium remains (Berzelius). According to Döbereiner, copper may be separated from palladium by reducing the latter metal with an alkaline formate.

*Atomic Weight of Palladium.*—Berzelius (Pogg. Ann. xiii. 435) determined the atomic weight of this metal in the same manner as that of iridium (iii. 321) by reducing potassio-palladious chloride, $2KCl.Pd''Cl^2$, in a current of hydrogen. As this salt cannot be dried without partial decomposition, the mixture of chloride of potassium and metallic palladium left after the ignition was weighed, as was also the palladium left after dissolving out the chloride of potassium with water. In one experiment, 0·575 grm. palladium were obtained to 0·809 grm. potassium-chloride, in another, 0·851 grm. palladium to 1·192 potassium-chloride. If $KCl = 74·5$, the mean of these experiments gives $Pd = 126·26$ or nearly 126.

**PALLADIUM, FLUORIDE OF.** $Pd''F^2$.—Formed as a brown precipitate on adding hydrofluoric acid to a concentrated solution of palladious nitrate. On evaporating to dryness, there remains a brown earthy mass, only a small portion of which is dissolved by water. It is not altered by ignition, is sparingly soluble in hydrofluoric acid, and dissolves very slowly in caustic ammonia, forming a colourless liquid, which may be evaporated by heat, and ultimately deposits fluoride of palladium as a colourless crystalline salt, which may be heated to 100° without decomposition, but decomposes at a higher temperature, leaving a grey-brown powder.

*Ammonio-palladious fluoride* is obtained as a brown radiate mass by dissolving palladious fluoride in boiling aqueous ammonia, and evaporating.

*Potassio-palladious fluoride* is precipitated on mixing palladious nitrate with fluoride of potassium, as a light yellow powder sparingly soluble in water.

*Sodio-palladious fluoride* is obtained in like manner and possesses similar properties.

**PALLADIUM, IODIDE OF.** $Pd''I^2$.—Palladium-foil turns black when an alcoholic solution of iodine is evaporated to dryness upon it; this reaction distinguishes palladium from platinum, which remains bright when thus treated (Berzelius). Similarly, palladium-foil heated in iodine vapour becomes covered with coloured films, and afterwards turns brown; the application of heat or treatment with ammonia restores its brightness. Iodine heated in a glass tube with finely-divided palladium, combines but imperfectly with it; and again, when palladium-foil is boiled with iodine and water, or with hydriodic acid and nitric acid, part of it remains unaltered. (Lassaigne.)

Iodide of palladium is obtained in the form of a black, tasteless, and inodorous mass, by precipitating a palladious salt with iodide of palladium, washing with boiling water, and drying the black gelatinous flakes for 24 hours in vacuo (Lassaigne, J. Chim. med. xi. 57). It gives off its iodine between 300° and 360°. Boiling potash decomposes it with separation of a black powder consisting of palladious oxide. It is insoluble in water, alcohol, ether, and aqueous hydriodic acid (thereby distinguished from platinum) (Lassaigne). This compound serves for the quantitative estimation of iodine (iii. 296).

**PALLADIUM, OXIDES OF.** The *protoxide* or *Palladious oxide*, $Pd''O$, is obtained in the anhydrous state by decomposing nitrate of palladium at a moderate heat, or by heating a palladious salt with carbonate of potassium to commencing redness, and exhausting the residue with water. It is a dark grey or black powder, sparingly soluble in acids, and is reduced to the metallic state at a bright red heat.

*Palladious hydrate* is obtained as a dark brown precipitate by mixing the solution of a palladious salt with excess of potassic or sodic carbonate. It gives off its water at a moderate red heat. It is easily soluble in acids.

The *dioxide* or *Palladic oxide*, $Pd^{iv}O^2$, is not known in the separate state. From a solution of palladic chloride alkalis and alkaline carbonates throw down a brown precipitate consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature. From hot solutions, a black precipitate is obtained containing the anhydrous dioxide. The hydrate dissolves slowly in acids, forming yellow solutions. In strong hydrochloric acid it dissolves without decomposition, forming *potassio-palladic chloride* arising from admixed potash; with dilute hydrochloric acid, on the contrary, it gives off chlorine.

**PALLADIUM, SELENIDE OF.** $Pd''Se$.—The two bodies unite easily, the combination being attended with evolution of heat. The product is a grey, infusible compound, which when heated in the blowpipe flame, gives off selenium, and leaves a greyish-white, brittle, crystalline, metallic bead containing selenium. (Berzelius.)

**PALLADIUM, SULPHIDE OF.** $Pd''S$.—Palladium and sulphur heated together unite, with incandescence, forming a bluish-white, metallic-shining, very hard compound, having a shining laminated fracture, and melting at the same temperature as silver. By precipitating a palladium-salt with sulphydric acid or an alkaline sulphide, sulphide of palladium is obtained as a black powder, having a bluish tinge and semi-metallic lustre. Sulphide of palladium heated to redness in the air oxidises very slowly, forming a basic sulphate or oxysulphate of palladium. Heated in a stream of chlorine gas, it forms chloride of sulphur and dichloride of palladium.

**PALLADIUM-BASES, AMMONIACAL.** (Vanquelin, Ann. Chim. lxxxviii. 167.—Fischer, Schw. J. li. 192.—Ann. Ch. Pharm. lxiv. 260.—Fehling, *ibid.* xxxix. 116.—Hugo Müller, *ibid.* lxxxvi. 341.)—*a.* A moderately concentrated solution of dichloride of palladium treated with a slight excess of ammonia, yields a beautiful flesh-coloured or rose-coloured precipitate, consisting of $N^2H^6Pd''Cl^2$ (Vanquelin, Fehling, Fischer). This precipitate dissolves in a larger excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition (Fehling, Fischer). This yellow modification is likewise obtained by heating the red compound in the moist state to 100°, or in the dry state to 200°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. For this reason, Hugo Müller regards the red compound as *ammonio-chloride of palladium*, $2NH^3.Pd''Cl^2$, and the yellow as *chloride of palladammonium*, $N^2H^6Pd''.Cl^2$. The yellow compound, digested with water and oxide of silver, yields the *oxide of palladammonium*, or *palladamine*, $N^2H^6Pd''O$. This compound is a strong base, analogous to oxide of platammonium (*q. v.*). It is soluble in water, to which it communicates a strong alkaline taste and reaction. By evaporating the solution in vacuo, the base is obtained in the form of a crystalline mass, which absorbs carbonic acid rapidly from the air, especially when moist. It unites with acids, forming definite salts. Its solution precipitates the salts of silver and copper, and an excess of it does not redissolve the precipitates. *Sulphite of palladammonium*, $N^2H^6Pd''.SO^3$, is formed by saturating the solution of the oxide with sulphurous acid, or by the action of that acid on the yellow chlorine-compound: it crystallises in orange-yellow octahedrons. The *sulphate*, $N^2H^6Pd''.SO^4$, crystallises in a similar manner. The *nitrate*, *iodide*, and *bromide* have also been formed. The *fluoride* is obtained by adding the chloride to a solution of fluoride of silver. (H. Müller.)

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β. The compound $4NH^3.Pd''Cl^2$ (called by Müller, *chloride of pallad-diamine*), which may be formulated as a chloronitride $\left.\begin{matrix}H^{12}\\ Pd''\end{matrix}\right\}\begin{matrix}N^4\\ Cl^2\end{matrix}$ or as *chloride of ammopalladammonium*, $\left.\begin{matrix}H^4\\ Pd''\\ (NH^4)^2\end{matrix}\right\}N^2.Cl^2$, separates from the ammoniacal solution of chloride of palladammonium, in colourless, oblique rhombic prisms, which at 200° give off half their ammonia and are reduced to $N^2H^6Pd''Cl^2$ (Fehling). The corresponding *iodide* and *bromide* are likewise obtained by treating the solutions of iodide and bromide of palladium or palladammonium with ammonia. They both crystallise readily. The *fluoride* is obtained by adding ammonia to the solution of chloride of palladammonium in fluoride of silver, and evaporating: it forms oblique rhombic prisms. The *silico-fluoride* is obtained in crystalline scales on adding hydrofluosilicic acid to any soluble salt of palladammonium. The *oxide* $N^4H^{12}Pd^2O^2 = \left.\begin{matrix}H^{12}\\ Pd''\end{matrix}\right\}\begin{matrix}N^4\\ O\end{matrix}$ is obtained by decomposing the solution of the chloride with oxide of silver,—or better, the sulphate with hydrate of barium. A strongly alkaline solution is thereby formed, which, on evaporation, leaves the hydrated oxide in the form of a crystalline mass, though not quite pure. The solution precipitates the salts of aluminium, iron, cobalt, nickel, and copper, but not those of silver; expels ammonia from chloride of ammonium, on boiling; and absorbs carbonic acid from the air. The *carbonate* obtained in this manner, or by decomposing the chloride with carbonate of silver, or the sulphate with carbonate of barium, crystallises in shining, colourless prisms, which turn yellow at a little above 100°; the solution of this salt is strongly alkaline, and gives copious precipitates with salts of calcium, barium, copper, and silver. The *sulphite*, $\left.\begin{matrix}H^{12}\\ Pd''\\ (SO)''\end{matrix}\right\}\begin{matrix}N^4\\ O^2\end{matrix}$ obtained by direct combination or by the action of ammonia on sulphite of palladammonium, forms small prismatic crystals, sparingly soluble in water, insoluble in alcohol, and turning yellow at about 392°. The *sulphate*, obtained by treating palladious sulphate with excess of ammonia, forms small colourless prisms, easily soluble in water, but insoluble in alcohol. (Hugo Müller.)

**PALLADIUM-BASES, ORGANIC.** (Hugo Müller, *loc. cit.*)—α. *Ethyl-compounds.* When ethylamine is added to a solution of palladious chloride, a yellow precipitate is formed containing $(C^2H^7N)^2.Pd''Cl^2$. It dissolves in ethylamine, forming a colourless solution, which on addition of hydrochloric acid yields a pale yellow precipitate, afterwards becoming dark yellow and crystalline: this precipitate is metameric with the preceding, and appears to consist of chloride of palladethylammonium $\left.\begin{matrix}(C^2H^5)^2\\ Pd''\\ H^4\end{matrix}\right\}N^2Cl^2$. A solution of this yellow salt in excess of ethylamine deposits colourless prisms of the salt $\left.\begin{matrix}(C^2H^5)^2\\ Pd''\\ H^2(C^2H^8N)^2\end{matrix}\right\}N^2Cl^2$ or $\left.\begin{matrix}(C^2H^5)^4\\ Pd''\\ H^8\end{matrix}\right\}\begin{matrix}N^4\\ Cl^2\end{matrix}$.

When the chloride of palladammonium (p. 328) is treated with aqueous ethylamine it quickly becomes decolorised and dissolves on gentle heating, to a colourless liquid, which on cooling deposits colourless crystals of the salt $\left.\begin{matrix}(C^2H^8N)^2\\ Pd''\\ H^4\end{matrix}\right\}N^2Cl^2$ or $\left.\begin{matrix}(C^2H^5)^2\\ Pd''\\ H^{10}\end{matrix}\right\}\begin{matrix}N^4\\ Cl\end{matrix}$. Müller's *chloride of paladethyldiamine.*

β. *Phenyl-compound.*—On adding aniline suspended in water to a solution of palladious chloride, a pale yellow crystalline precipitate, insoluble in excess of aniline, is formed, probably consisting of chloride of palladio-phenylammonium, $H^4(C^6H^5)^2Pd''N^2.Cl^2$. The corresponding iodine-compound is obtained as a yellow crystalline powder on mixing finely divided iodide of palladium with aniline suspended in water.

**PALMIC ACID.** Syn. with Ricinelaïdic Acid.

**PALMIN.** Syn. with Ricinelaïdin.

**PALMITAMIDE.** $C^{16}H^{33}NO = \left.\begin{matrix}C^{16}H^{31}O\\ H^2\end{matrix}\right\}N$. (H. Carlet, Bull. Soc. Chim. 1859, p. 175.)—This compound is obtained by heating palmitate of ethyl with alcoholic ammonia for twenty to twenty-five days in a sealed tube immersed in a salt-bath, and is purified by re-crystallisation from hot alcohol, and repeated washing with cold ether. It melts (or solidifies) at 101·5°. By heating in a sealed tube with alcoholic potash, it is resolved into palmitic acid (solidifying at 59·5°) and ammonia.

The *margaramide* which Boullay obtained by the action of ammonia on olive-oil probably consisted chiefly of oleamide (p. 192).

**PALMITIC ACID.** $C^{16}H^{32}O^2 = \left.\begin{matrix}C^{16}H^{31}O\\ H\end{matrix}\right\}O$. *Cetylic acid. Ethalic acid. Olidic acid.* (Chevreul, *Recherches sur les corps gras*, p. 59.—Dumas and Stas, Ann. Ch. Phys. [2] lxxiii. 113.—Varrentrapp, Ann. Ch. Pharm. xxxv. 209.—Frémy, *ibid.* xxxvi. 44.—Stenhouse, *ibid.* xxxvi. 50.—L. Smith, *ibid.* xlii. 241.—Sthamer and Meyer, *ibid.* xliii. 335.—H. Schwarz, *ibid.* lx. 69.—Heintz, see references already given iii. 1069.—v. Böck, J. pr. Chem. xlix. 295.—Berthelot, Ann. Ch. Phys. [3] xli. 216, 432; xlvii. 297.—Maskelyne, Chem. Soc. Qu. J. viii. 1.—Gm. xvi. 350.—Gerh. ii. 795.)

This acid is universally distributed in the fats of the animal and vegetable kingdoms. It occurs: *α*. Combined with glycerin, in large quantities, in palm-oil (Frémy); in Chinese tallow, the fat of *Stillingia sebifera* (Maskelyne); in Japan wax (Sthamer); in the wax of *Myrica sebifera* (Moores).—*β*. Combined with ethal, in spermaceti (L. Smith).—*γ*. In the melissin of bees-wax, as palmitate of melissyl, $C^{16}H^{31}(C^{30}H^{61})O^2$ (Brodie).—*δ*. In the free state in partially decomposed fats, especially in palm-oil.

Chevreul's *margaric acid*, which, as already observed (iii. 852), is a mixture of palmitic acid with 10 per cent. stearic acid, is formed in large quantities in the saponification of spermaceti, of human, jaguar, and goose-fats, and of dolphin and train oils; in small quantity, together with much stearic acid, by the saponification of butter, hog's lard, beef-suet, and mutton-suet. The other varieties of the so-called margaric acid also consist of palmitic acid more or less pure: hence, many of the older observations relating to margaric acid really apply to palmitic acid.

*Formation.*—1. By the saponification of palmitin, spermaceti, and melissin.—2. By heating ethal (cetylic hydrate) with potash-lime (Dumas and Stas):

$$\underset{\text{Hydrate of cetyl.}}{C^{16}H^{34}O} + KHO = \underset{\text{Palmitate of potassium.}}{C^{16}H^{31}KO^2} + H^4.$$

3. Together with acetic acid, by melting oleic acid (Varrentrapp), or elaïdic acid (Meyer), with potassic hydrate:

$$\underset{\text{Oleic acid.}}{C^{18}H^{34}O^2} + 2KHO = \underset{\text{Palmitate of potassium.}}{C^{16}H^{31}KO^2} + \underset{\text{Acetate of potassium.}}{C^2H^3KO^2} + H^2.$$

Oleic acid appears also to be converted into palmitic acid when fats or fatty substances are left for a long time in moist earth, or in other moist situations excluded from the air, the fat then becoming harder and more brittle. When castor-oil is distilled with, excess of alkali (iii. 144), there remains in the residue, together with sebacic acid, an oily acid which on standing deposits a large quantity of solid fat having the melting point and composition of palmitic acid.

4. Together with cetylene, by the dry distillation of cetylic palmitate (cetin) (L. Smith):

$$\underset{\text{Cetin.}}{\left.\begin{matrix}C^{16}H^{31}O\\ C^{16}H^{33}\end{matrix}\right\}O} = \underset{\text{Palmitic acid.}}{\left.\begin{matrix}C^{16}H^{31}O\\ H\end{matrix}\right\}O} + \underset{\text{Cetylene.}}{C^{16}H^{32}}.$$

*Preparation.* *a. From Palm-oil*—Palm-oil is saponified with caustic potash; the soap thus obtained is decomposed, and the separated fatty acid is purified by crystallisation from alcohol (Frémy). Stenhouse dissolves the six or eight times crystallised acid in caustic potash, and precipitates it with an acid. Schwarz saponifies palm-oil with caustic potash, dissolves the soap in hot alcohol, allows the solution to cool, and purifies the crystalline nodules which separate, by repeated crystallisation from alcohol, with aid of animal charcoal. The crystals, when decomposed by hydrochloric acid, yield palmitic acid, which must again be crystallised from alcohol.

*β. From Japan Wax.*—The wax is saponified by fusing it with half its weight of hydrate of potassium, and the soap is dissolved in water and salted out. The soda-soap thus formed is dissolved in warm water and allowed to cool; it is then pressed, again dissolved in water, and the solution is heated to the boiling point, and decomposed with chloride of calcium. The lime-soap, after being washed and dried, is freed from unsaponified wax by means of ether, and decomposed by hydrochloric acid. The separated fatty acid is crystallised, first from alcohol, afterwards from a mixture of alcohol and ether, and is lastly washed with cold alcohol. (Sthamer.)

*γ. From Chinese Wax.*—The wax is saponified with alcoholic potash; the alcohol is distilled off, after addition of water, and the soap is decomposed with sulphuric acid. The separated fatty acid is then strongly pressed, and the press-cake is moistened with alcohol, and again pressed several times. The remaining mass is crystallised from hot alcohol until it exhibits the melting point of palmitic acid. (Maskelyne.)

*δ*. From *Coffee-beans.*—The powdered beans are extracted with ether containing water, and the ether is evaporated; the remaining yellow bitter fat is freed from the various acids of coffee, and from caffeïne, by shaking it repeatedly with one-fifth its volume of water and drawing off the aqueous layer of liquid, and is afterwards saponified with caustic potash. The soap is salted out, dissolved in water, and decomposed by dilute sulphuric acid; and the mixture of oleic and palmitic acids is converted into lead-salts by boiling the acids with carbonate of sodium, dissolving the soda-soap in alcohol, and precipitating with neutral acetate of lead. The lead-salts are boiled with alcohol, which dissolves them completely; but on cooling and partly evaporating the solution, the palmitate of lead separates in the form of a white powder, whilst the oleate remains in solution. The former is collected, washed with alcohol containing water, and decomposed by sulphydric acid under ether-alcohol. The palmitic acid remaining behind, when the filtrate is evaporated, is obtained with a melting point of 58·5° by five times repeated crystallisation. (Roehleder, Ann. Ch. Pharm. vii. 228.)

ε. *From Oleic acid.*—Oleic acid is saponified by a slight excess of hydrate of potassium, with addition of a little water; a quantity of hydrate of potassium, equal to twice the weight of the oleic acid is then added; and the mixture is heated, with constant stirring, until the potash is melted, too great a heat being prevented by the occasional addition of a few drops of water, so that the mass may not blacken, but only assume a brown-yellow colour. As soon as the potash is melted, and hydrogen gas is evolved, the fire is removed, and the mass is thrown into not too large a quantity of water, when the soap which has been formed separates and floats on the surface. The soap is removed, dissolved several times in water, and salted out, and afterwards decomposed by dilute hydrochloric acid: the palmitic acid thus separated is purified by crystallisation from alcohol. (Varrentrapp.)

ζ. *From Ethal.*—Ethal, mixed with five or six parts of potash-lime, is heated to 210°—220° (263°—275°, according to Heintz), in a metal-bath for five or six hours, or so long as hydrogen is evolved; the residue is suspended in water; and an excess of hydrochloric acid is added, whereby the palmitic acid is separated in white flocks. After allowing the mixture to boil, the acid is washed, then boiled for half an hour with excess of hydrate of barium, and evaporated to dryness. The ethal remaining undecomposed is taken up by ether; the residue is decomposed by hot hydrochloric acid; and the separated acid is washed and dissolved in ether, to remove traces of undecomposed barium-salt (Dumas and Stas). The palmitic acid thus obtained still requires to be freed from stearic, myristic, and lauric acids, which are produced at the same time. (Heintz.)

The fatty acids obtained by saponifying fats, or by heating with potash-lime, and decomposing the soaps (and freed from oleic acid by the method already described, iii. 474), admit of separation into two distinct portions—inasmuch as when they are dissolved in hot alcohol, a mixture of the more difficultly fusible acids containing a high percentage of carbon, especially palmitic, stearic, and likewise arachidic acid, if present, crystallises out on cooling;—and by pressing the crystals, moistening with alcohol, and again pressing, they may be obtained separately, while a smaller portion of the same acids, together with the more easily fusible myristic and lauric acids, remains in solution, and may be separated by methods already described (iii. 474, 1070).

When the fats contain no acids with a higher percentage of carbon than palmitic acid, and more especially no stearic or arachidic acid, or only small quantities thereof, they may be crystallised from alcohol until the crystals melt at 62°, and are then to be examined as to their purity by the method given at p. 1070, vol. iii. In the contrary case, the whole of the acids are dissolved in such a quantity of alcohol, that nothing crystallises out on cooling; the solution is precipitated two or three times with a quantity of acetate of magnesium equal to about $\frac{1}{10}$th of the fatty acids; and the successive precipitates are separated by filtering and pressing. These precipitates contain the whole of the stearic acid, provided the fat does not contain too large a quantity of it, together with a relatively small quantity of palmitic acid. The mother-liquors, diluted with a large quantity of hot water, and left to cool, deposit the palmitic acid, which is collected, examined as to its purity, and purified either by recrystallisation from alcohol, or by again precipitating it with small portions of acetate of magnesium (Heintz) In a later process Heintz precipitates the sodium-salt, instead of the alcoholic acid, with acetate of magnesium, in the manner above described.

For the older methods of preparation, whereby the so-called margaric acid was obtained, together with stearic and oleic acids, see *Gmelin's Handbook*, xvi. 355.

*Properties.*—Palmitic acid is a colourless solid body without taste or smell, lighter than water. It is insoluble in *water*, but dissolves abundantly in boiling *alcohol* or *ether*. The solutions are acid, and when concentrated, solidify in a mass on cooling. When dilute they yield the acid in tufts of slender needles. It melts at 62°, and solidifies on cooling in a mass of shining nacreous laminæ. According to Frémy, palmitic acid which has been heated to 250°, crystallises from alcohol in small very hard crystals.

Palmitic acid may be melted together with *lauric* and *myristic acids*. In certain proportions the mixtures are not separable by crystallisation from alcohol or ether: they exhibit the following characters on melting and solidifying (Heintz):

| A mixture of— | | Melts at | Mode of Solidifying. |
|---|---|---|---|
| Palmitic acid. | Lauric acid. | | |
| 10 | 90 | 41·5° | Uncrystallised. |
| 20 | 80 | 37·1° | Finely crystallised, indistinct. |
| 30 | 70 | 38·3° | Small-leaved, crystalline. |
| 40 | 60 | 40·1° | Splendid large laminæ. |
| 50 | 59 | 47·0° | Opaque, scarcely crystalline. |
| 60 | 40 | 51·2° | Granular, distinctly scaly. |
| 70 | 30 | 54·5° | More distinctly scaly. |
| 80 | 20 | 57·4° | Still more distinctly scaly. |
| 90 | 10 | 59·8° | Crystalline scales. |

| A mixture of— | | Melts at | Solidifies at | Mode of Solidifying. |
|---|---|---|---|---|
| Palmitic acid. | Myristic acid. | | | |
| 95 | 5 | 61·1° | 58° | Crystalline scales. |
| 90 | 10 | 60·1° | 55·5° | ,, ,, |
| 80 | 20 | 58° | 53·5° | Scales with slight admixture of needles. |
| 70 | 30 | 54·9° | 51·3° | Very delicate needles. |
| 60 | 40 | 51·5° | 49·5° | Uneven, uncrystallised. |
| 50 | 50 | 47·8° | 45·3° | Large laminæ. |
| 40 | 60 | 47° | 43·7° | Indistinctly lamellar. |
| 35 | 65 | 46·5° | . . | Uncrystallised, opaque. |
| 32·5 | 67·5 | 46·2° | 44° | ,, ,, |
| 30 | 70 | 46·2° | 43·7° | ,, ,, |
| 20 | 80 | 49·5° | 41·3° | Uncrystallised. |
| 10 | 90 | 51·8° | 45·3° | Long needles. |

A mixture of 30 per cent. myristic and 70 per cent. lauric acid melts at 35·1°; and when to 20 parts of this mixture, from 1 to 100 parts palmitic acid are added, the melting-points of the resulting mixtures are altered, according to Heintz, as follows:—On addition of,

| Palmitic acid. | The melting point is— | Palmitic acid. | The melting point is— |
|---|---|---|---|
| 1 part . . . | 33·9° | 6 parts . . . | 34·6° |
| 2 ,, . . . | 33·1° | 7 ,, . . . | 35·3° |
| 3 ,, . . . | 32·2° | 8 ,, . . . | 36° |
| 4 ,, . . . | 32·7° | 9 ,, . . . | 37·3° |
| 5 ,, . . . | 33·7° | 10 ,, . . . | 38·8° |

The mixtures with 9 and 10 parts palmitic acid solidify in delicate needles, the others uncrystallised. (Heintz.)

For the mode of solidifying of mixtures of palmitic and stearic acids, see STEARIC ACID.

The composition of palmitic acid is as follows:

| | *Calculation.* | | Frémy. | Stenhouse. | Schwarz. | Sthamer. | Varrentrapp. | Brodie. | Heintz. | |
|---|---|---|---|---|---|---|---|---|---|---|
| $C^{16}$ | 192 | 75·0 | 74·3 | 74·54 | 74·9 | 74·43 | 74·41 | 74·97 | 74·89 | 74·88 |
| $H^{32}$ | 32 | 12·5 | 12·4 | 12·48 | 12·5 | 12·55 | 12·26 | 12·46 | 12·51 | 12·60 |
| $O^{2}$ | 32 | 12·5 | 13·3 | 12·98 | 12·6 | 13·02 | 13·33 | 12·57 | 12·60 | 12·52 |
| | 256 | 100·0 | 100·0 | 100·00 | 100·0 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Palmitic acid heated in a dish boils and evaporates without residue (Dumas and Stas). On distillation it passes over almost entirely unchanged, giving off only a little oil and leaving (Frémy) a slightly coloured residue, which melts at 72°, and probably consists of palmitone (Maskelyne); the melting point of the distillate is lowered from 58° to 57°, and the percentage of carbon somewhat increased (Schwarz), but after recrystallisation, the acid remains unaltered. (Frémy.)

When gently heated in contact with the *air*, it is but slightly altered, but at higher temperatures it takes fire and burns with a bright smoky flame like other fats. It absorbs *ozone* but slowly, even in presence of an alkali, much of the acid remaining unaltered even after exposure for several weeks to ozonised air. Carbonic acid is formed in the oxidation, but no other acid. (Gorup-Besanez, Ann. Ch. Pharm. cxxv. 215.)

Palmitic acid is not attacked by *chlorine* at ordinary temperatures, but at 100° hydrochloric is evolved and oily substitution-products are formed.—Distilled with *lime*, either anhydrous or hydrated, it yields palmitone and carbonate of calcium. (Piria. Maskelyne.)

$$2C^{16}H^{32}O^2 \quad = \quad C^{31}H^{62}O \quad + \quad CO^2 \quad + \quad H^2O$$

It is not altered by heating to 275° with *potash-lime* in a closed vessel; if air be admitted, a little butyric acid is formed, with separation of charcoal, but the greater part of the palmitic acid remains unaltered (Heintz). When palmitic acid is heated to low redness with excess of potash-lime, gaseous and liquid olefines are produced. (Cahours, Compt. rend. xxxi. 142.)

Palmitic acid heated with *alcohols* form compound ethers.

**Palmitates.** The formula of the neutral palmitates is $C^{16}H^{31}MO^2$ (or perhaps, $C^{32}H^{62}M^2O^2$) for monatomic, and $C^{32}H^{62}M''O^2$ for diatomic metals. The alkali-metals also form acid palmitates analogous to the acid acetates, butyrates, &c., having the composition $C^{16}H^{31}MO^2.C^{16}H^{32}O^2$, or rather $C^{32}H^{63}MO^4$, the acids of the series $C^nH^{2n}O^2$ being most probably dibasic. The neutral palmitates of potassium and sodium are soluble in water and in alcohol; all the rest are insoluble. The insoluble neutral palmitates are obtained by precipitating the solutions of the corresponding metallic salts with an alcoholic solution of palmitate of potassium or sodium.

An *acid palmitate of ammonium*, probably $C^{32}H^{63}(NH^4)O^4$, is deposited from solutions of palmitic acid even in a large excess of ammonia; it is insoluble in cold water. (Frémy.)

*Potassium-salts.* The *neutral-salt*, $C^{16}H^{31}KO^2$, obtained by melting palmitic acid with carbonate of potassium and exhausting with boiling alcohol, crystallises from the alcoholic solution in white pearly scales, fusible without decomposition or loss of weight. It dissolves in a small quantity of water, but is decomposed by a large quantity; perfectly soluble in alcohol, insoluble in ether.—The *acid salt*, $C^{32}H^{63}KO^4$, is precipitated on mixing a solution of 1 pt. of the neutral salt in 20 pts. boiling water with 1000 pts. cold water. By dissolving the dried precipitate in boiling alcohol, and leaving the solution to cool, the acid salt is obtained in small pearly scales. Water added to the alcoholic solution precipitates a more highly acid salt (Chevreul). Schwarz, by saponifying palm-oil with potash, and crystallising the soap from alcohol, obtained an acid potassic palmitate in nodules which melted at 100°.

*Sodium-salts.* The *neutral salt*, $C^{16}H^{31}NaO^2$, prepared like myristate of sodium (iii. 1072), forms broad pearly laminæ more easily decomposed by water than the potassium-salt (Dumas and Stas). According to Heintz, it separates from alcoholic solution in the form of a jelly, which, on standing with a sufficient quantity of alcohol, changes to colourless laminæ. The *acid salt*, $C^{32}H^{63}NaO^4$, obtained by dissolving the neutral salt in 1500 pts. hot water and leaving the solution to cool, is white, tasteless, more fusible than the neutral salt, insoluble in water, easily soluble in hot alcohol. (Chevreul.)

The *barium-salt*, $C^{32}H^{62}Ba''O^4$, is a white, pearly, crystalline powder, which decomposes before melting. The *magnesium-salt*, $C^{32}H^{62}Mg''O^4$, is a snow-white, loose crystalline precipitate, which dissolves in boiling alcohol, and crystallises almost completely on cooling, in microscopic rectangular laminæ.

The *copper-salt*, $C^{32}H^{62}Cu''O^4$, is a pale green-blue, very loose powder, composed of microscopic laminæ. It melts, when heated, to a green liquid which rapidly decomposes. The *lead-salt*, $C^{32}H^{62}Pb''O^4$, forms snow-white microscopic scales, which melt at 108° (Maskelyne), between 110° and 112° (Heintz), and solidify to a white opaque amorphous mass. By heating this salt or the acid with basic acetate of lead, basic palmitates of lead are obtained. The *silver-salt*, $C^{16}H^{31}AgO^2$, is thrown down from cold solutions as a somewhat gelatinous precipitate, which is blackened by light in the moist, but not in the dry state (Varrentrapp). It appears amorphous even when highly magnified (Heintz). It dissolves slightly in water (Varrentrapp). From a solution in warm aqueous ammonia it separates in indistinct scales. (v. Borck.)

**PALMITIC ETHERS.** a. Containing the alcoholic-radicles $C^nH^{2n+1}$.—*Methylic Palmitate*, $C^{17}H^{34}O^2 = C^{16}H^{31}(CH^3)O^2$, obtained by heating palmitic acid with methylic alcohol in a sealed tube to 200°—250°, forms crystals which melt at 28° and solidify at 22°. (Berthelot.)

*Ethylic Palmitate, Palmitic* or *Ethalic ether*, $C^{18}H^{36}O^2 = C^{16}H^{31}(C^2H^5)O^2$, is obtained by passing hydrochloric acid gas into a saturated alcoholic solution of palmitic acid (Frémy, Heintz); also by heating palmitic acid with ethylic alcohol to 200°—250°, or with ethylic ether to 360° (Berthelot). It crystallises in prisms, melts at 24·2°, and solidifies in a foliated mass on cooling. When crystallised from an alcoholic solution at 5° to 10°, it forms long flattened needles.

*Amylic Palmitate*, $C^{21}H^{42}O^2 = C^{16}H^{31}(C^5H^{11})O^2$, is obtained by similar processes; also when palmitin is boiled with amylic alcohol containing amylate of sodium (Duffy, Chem. Soc. Qu. J. v. 314). It is soft, non-crystalline, and melts at 9° (Berthelot); at 13·5°. (Duffy.)

*Cetylic Palmitate*, $C^{32}H^{64}O^2 = C^{16}H^{31}(C^{16}H^{33})O^2$, constitutes the principal part of the solid portion (*cetin*) of spermaceti.

*Myricylic Palmitate*, $C^{46}H^{92}O^2 = C^{16}H^{31}(C^{30}H^{61})O^2$, is contained in considerable quantity in the portion of bees-wax which is insoluble in boiling alcohol (see MYRICIN, iii. 1069).

β. PALMITATES OF GLYCERYL or PALMITINS. Palmitic acid forms three compounds with glycerin, viz.:

*Monopalmitin*, $C^{19}H^{38}O^4 = \left.\begin{matrix}(C^3H^5)''' \\ H^2.C^{16}H^{31}O\end{matrix}\right\}O^3$, is obtained by heating a mixture of glycerin and palmitic acid to 200° for 24 hours. It forms radiating colourless prisms, melts at 58°, and distils in the barometric vacuum without alteration. Heated in contact with the air, it yields acrolein. It dissolves readily in ether. It is saponified by oxide of lead, yielding glycerin and palmitic acid.

*Dipalmitin*, $C^{35}H^{68}O^5 = \left.\begin{matrix}(C^3H^5)''' \\ H(C^{16}H^{31}O)^2\end{matrix}\right\}O^3$, is produced by heated palmitic acid and glycerin together to 100° for 14 hours. It forms colourless tables or needles, which melt at 50°, yield acrolein when heated in the air, and burn without residue. It is rapidly saponified by oxide of lead at 100°.

*Tripalmitin*, $C^{51}H^{98}O^6 = \left.\begin{matrix}(C^3H^5)''' \\ (C^{16}H^{31}O)^3\end{matrix}\right\}O^3$, is obtained by heating a mixture of 1 pt. monopalmitin and 10 pts. palmitic acid to 250° for 28 hours. It is solid, melts at 60°, solidifies at 46°, and is saponified by oxide of lead.

*Natural palmitin*, occurring in the fats which yield palmitic (or margaric) acid, by saponification, is isomeric, if not identical, with tripalmitin. It is crystallisable, sparingly soluble in alcohol, and dissolves in all proportions in ether. According to Duffy (*loc. cit.*), it exhibits three distinct melting points, viz. 46°, 61·7° and 62·8°, corresponding to three different physical modifications (see GLYCERIDES, ii. 879). It solidifies at 45·5°.

Palmitin exists in palm-oil, Japan wax (Sthamer), human fat (Heintz), and coffee-berries (Rochleder). It is extracted from palm-oil by pressure, and the residue is washed with boiling alcohol, and crystallised several times from ether.

γ. PALMITATE OF MANNITYL. *Dipalmito-mannitan, Mannite mono-palmitique*, $C^{38}H^{72}O^7 = \left.\begin{matrix}(C^6H^8)^{vi} \\ (C^{16}H^{31}O)^2 \\ H^3\end{matrix}\right\}O^5$. To prepare this compound, palmitic acid is heated with mannite in a sealed tube to 120° for 15 to 29 hours, and the fatty layer which floats on the surface and solidifies on cooling, is melted in a water-bath, mixed with a little ether and with excess of slaked lime, heated for 10 minutes to 100°, and then exhausted with ether. If the product obtained by evaporating the ethereal solution reddens litmus, in must be once more treated with ether and lime.

Mannitic palmitate is a solid, white, neutral mass, resembling palmitin, and separating from ether in microscopic crystals. It melts to a wax when heated on platinum-foil, and volatilises almost undecomposed, charring only towards the end; the residue burns away. Water, at 240°, decomposes it in a few hours into mannitan and palmitic acid. Insoluble in water, soluble in ether. (Berthelot, Ann. Ch. Phys. [3] xlvii. 323.)

**PALMITIN.** See PALMITATES OF GLYCERYL (p. 334).

**PALMITONE.** $C^{31}H^{62}O = \left.\begin{matrix}C^{16}H^{31}O \\ C^{16}H^{31}\end{matrix}\right\}$ *Ethalone.* (Piria, Compt. rend. xxxiv. 140; Maskelyne, Chem. Soc. Qu. J. viii. 1.)—The acetone or ketone of palmitic acid. It was first obtained by Bussy, who called it *margarone*, but his product was probably mixed with stearone. To prepare it, palmitic acid is distilled with excess of slaked lime (Piria), or with one-fourth of its weight of quicklime (Maskelyne), and

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the product is purified by repeated crystallisation from boiling alcohol. It forms small, white, pearly scales or laminæ; melts at 84°, and solidifies at 80° to a highly electric mass (Maskelyne). It dissolves in *alcohol*, with greater facility as the alcohol is stronger (Piria). Easily soluble in *benzene*. (Maskelyne.)

It resists the action of *nitric acid* and of *potash-ley*, but is attacked and blackened by *nitrosulphuric acid* (Maskelyne). It does not unite with *acid sulphites of alkali-metals*. (Limpricht, Ann. Pharm. xciv. 246.)

**PALMITONIC ACID.** An acid of doubtful composition, said by Schwarz (Ann. Ch. Pharm. lx. 58) to be produced when palmitic acid is kept in a state of fusion for a long time in contact with the air. Schwarz supposes that under these circumstances a portion of the carbon and hydrogen of the palmitic acid is removed by oxidation, and an acid is left having the composition $C^{31}H^{31}O^4$ or $C^{31}H^{62}O^4$. (For a description of this supposed acid and its salts, see *Handwörterbuch d. Chem.* vi. 36.)

**PALMITYL.** $C^{16}H^{31}O$.—The hypothetical radicle of palmitic acid and its derivatives. The same term is sometimes, but improperly applied to cetyl, $C^{16}H^{33}$.

**PALM-OIL** or **PALM-BUTTER.** This fat, which in the fresh state consists mainly of tripalmitin with a small quantity of olein, is obtained from the fruit of certain kinds of palm, *Cocos butyracea* according to some authorities, *Avoira elais* according to others; it is imported from Cayenne and the coast of Guinea. It has the consistence of butter, an orange colour, and an odour somewhat like that of violets. The fresh oil melts at 27°, but as it gets stale, the melting point rises to 31° and even to 36°, in consequence of the resolution of the neutral fats into glycerin and fatty acids. Old palm-oil usually contains a considerable quantity of free palmitic acid, the decomposition being induced, according to Pelouze and Boudet, by the presence of a peculiar ferment. It gives off acid vapours when heated to 140° and above, and at 300° it boils, emitting the odour of acrolein, and yielding a distillate of fatty acids (Pohl). It dissolves in strong sulphuric acid, and the solution on standing deposits palmitic acid (Frémy). It dissolves slowly and incompletely in cold alcohol, but mixes in all proportions with ether; dissolves in oil of turpentine and oil of almonds, with separation of flocculent matters. (Guibourt, J. Chim. méd. i. 177.—Henry, J. Pharm. li. 241.)

Palm-oil is extensively used in the manufacture of soap and candles, also, mixed with tallow and a certain portion of caustic soda, for making railway grease (see *Richardson and Watts's Chemical Technology*, vol. i. pt. 3, p. 742). For the latter purpose the crude yellow oil is used, but for soap and candle making the colour must be removed. The bleaching may be effected by various processes, viz.: by the action of chloride of lime, of oxygen derived from peroxide of manganese and sulphuric acid, or from bichromate of potash and sulphuric acid;—by heating the oil in a close vessel to 110° C. (230° F.) by means of high-pressure steam; or to 100° C. (212° F.) in open vessels, so that it may be exposed to the action of air and light. This last is the most economical of all methods of bleaching palm-oil, and has almost entirely superseded the others. It is carried out as follows:

Several very large square or flat boxes or cisterns are prepared, either constructed simply of wood, or, better, lined with lead. These boxes, which are twelve inches deep, and are furnished at the bottom with a serpentine leaden tube in connection with a steam-boiler, must be so situated as to admit of the free access of air and light. After they have been filled up to the height of eight inches with water, palm-oil is introduced in sufficient quantity to form a layer two inches deep after being melted by the admission of the steam, the current of which must be regulated so as to afford a uniform temperature of 100°. At the expiration of ten or fifteen hours, the colour is destroyed, the length of time required depending very much on the power of the sun's rays. Palm-oil might perhaps be advantageously bleached by the tropical sun of Africa, before its importation into Europe. The bleaching may also be accelerated by blowing air through the melted oil. The method of bleaching with chromate of potassium and sulphuric acid is more expeditious than that just described, but it is also much more expensive. The oil, even after being subjected to the most effective process of bleaching, still retains a slight yellowish hue, but this colour is no longer perceptible in the soap made from it. (For further details see *Chemical Technology*, vol i. pt. 2, p. 410; also, *Ure's Dictionary of Arts*, &c., p. iii. 290.)

**PALM-SUGAR.** The juice of various kinds of palm yields a saccharine matter from which cane-sugar may be extracted. In Java, a black very hygroscopic sugar is obtained from the juice of *Arenga saccharifera* and of *Saguerus Rumphii*. Berthelot, (Compt. rend. xlvi. 1276) has extracted cane-sugar from the latter. The so-called Ingar or Lontar sugar of India is prepared from the flower-stalks of *Borassus flabellifer*; it is likewise hygroscopic, and is said to be purgative when taken in large quantity.

**PALM-WAX.** *Cera de Palma.*—This wax is the produce of *Ceroxylon andicola*, a species of palm indigenous in the tropical regions of America. The entire stem of the tree, which is two feet thick and fifty feet high, is covered with a layer of wax; this is removed by scraping, and purified with hot water, in which it does not melt, but collects in a soft state on the surface. It is mixed with a little tallow to render it less brittle, and formed into balls, in which state it is sent into commerce; it is used in South America for making candles.

Palm wax unmixed with tallow is dark yellow, somewhat translucent, and has a conchoïdal fracture. It becomes strongly electric by friction, melts at a temperature somewhat above the boiling point of water, and takes fire at a somewhat higher temperature, burning with a bright smoky flame. It dissolves gradually but completely in caustic alkalis. It is likewise soluble in ether, and the solution when left to evaporate deposits the wax in crystals resembling carbonate of sodium. Hot alcohol resolves it into two distinct substances, a true wax and a resin. The former separates as a jelly from the cooling alcoholic solution, and may be freed from adhering resin by repeated solution in alcohol. It then melts below the boiling point of water, and closely resembles bees-wax in colour, and also in composition, as seen by the following comparison:

| *Palm-Wax.* | | | |
|---|---|---|---|
| Boussingault. | | Lewy. | *Bees-wax.* |
| 81·8 | 81·6 | 80·73 | 81·8 |
| 12·5 | 13·3 | 13·30 | 12·8 |
| 5·7 | 5·1 | 5·97 | 5·4 |
| 100·0 | 100·0 | 100·00 | 100·0 |

The resin, called **ceroxylin**, is obtained by evaporating the alcoholic liquor from which the jelly has been deposited, first to two-thirds, whereupon a little more wax separates from it, then to one-fourth, when the resin separates as a shining crystalline mass containing 83·4 per cent. carbon, 11·5 hydrogen, and 5·1 oxygen, agreeing with the formula $C^{20}H^{32}O$, which is also that of elemi-resin. Its melting point is above 100°. In the fused state it has the colour of amber, and splits in all directions as it cools. It is soluble in ether and in volatile oils.

Wax is likewise obtained from some other species of palm. The leaves of the Carnauba palm (*Corypha cerifera*), a native of northern Brazil, are coated with a thin layer of wax, which peels off as they dry. It is very brittle, easily pulverised, melts at 83·5°, dissolves in boiling alcohol and ether, and separates as a crystalline mass on cooling. Lewy found in it 80·4 per cent. carbon, 13·1 hydrogen, and 6·5 oxygen.

According to Teschemacher, considerable quantities of palm-leaves, probably of the dwarf palm (*Chamærops humilis*), are imported into the United States from Cuba and the other West Indian islands, for the use of hatters. These leaves are also coated with a thin layer of wax. Teschemacher obtained from a single leaf, by scraping with the finger, 90 grains of white pulverulent wax, and by exhaustion with alcohol, 300 grains more of a somewhat grey colour. This wax, when treated with a small quantity of alcohol, is resolved into two unequally soluble constituents.

**PALM-WINE.** An alcoholic beverage, prepared by fermentation of the saccharine juice of certain palms. In Amboina, the juice of *Arenga saccharifera* is used for this purpose. Palm-wine is likewise obtained from *Sagus raphia*, *Mauritia vinifera*, *Phœnix dactylifera*, *Cocos nucifera*, and others. In South America an intoxicating drink, called *Pulga* or *Pulque*, is prepared from the juice of *Fourorœa adorata*.

**PANABASE.** Syn. with TETRAHEDRITE.

**PANCREATIC JUICE.** A clear, ropy, colourless fluid, free from special morphological constituents, of no particular odour, with a distinctly alkaline reaction, flowing from the pancreas into the upper part of the duodenum, and of great use in digestion. The quantity secreted during a given time varies exceedingly, and depends mainly on the amount of food present in the alimentary canal. The percentage of total solids also varies greatly (from 2·3—9·9 for dogs); in general, the density of the liquid is in inverse ratio to the rapidity with which it is secreted. Pancreatic juice decomposes very speedily at the ordinary temperature, and then becomes rose-coloured on the addition of chlorine; a reaction which is lost at a later stage of decomposition.

In the case in which the total solids amounted to 9·924 per cent., the salts were ·886 per cent., and consisted chiefly of chloride of sodium (·736 per cent.), sulphates of sodium and potassium, phosphates of sodium, calcium and magnesium, and carbonate of calcium, with traces of iron.

The greater part of the organic matter may be thrown down by alcohol as a white flaky precipitate, which, when separated by filtration and dried, is easily redissolved in water. Heat (72°), mineral acids, tannin, &c., also produce precipitates. The aqueous solution of the alcohol-precipitate exhibits all the powers of the original secretion, and has been called **Pancreatin**. It is probably, however, a mixture, consisting principally of some protein-substance allied to casein. **Cohnheim** has separated from it a body, lacking protein characters, but converting starch into sugar with great energy, and **Danilewsky** (Virch. Arch. xxv. 279) attempts to show the existence of three special "ferments." He makes a pancreatic infusion by rubbing up with sand and cold water the pancreas of a dog killed six hours after a meal, and filtering; the filtrate acts on starch, albumin, and fats. Magnesia is added in excess, and the fluid again filtered; the filtrate acts on starch and albumin, but not at all on fat. To this second filtrate is carefully added one-third its volume of collodion, and the mixture is well shaken, the ether being allowed to evaporate. The precipitate, which is granular and not lumpy if the experiment has been well performed, is separated by filtration. The new filtrate acts upon starch, but not on albumin. The precipitate is washed with spirit, treated with a mixture of alcohol and ether, and filtered. The undissolved portion is washed with ether, dissolved in water, and again filtered. The filtrate, which gives no decided protein reaction, has no action on starch; but, when possessing a feebly alkaline reaction, readily dissolves fibrin. Pancreatic juice also contains extractive matters, and some fat. Leucine, in company with tyrosine, is found abundantly in the substance of the gland, and has also been detected in the secretion. M. F.

**PAPAVERINE.** $C^{20}H^{21}NO^4$. (G. **Merck** [1850], Ann. Ch. Pharm. lxvi. 125; lxxiii. 50.—**Anderson**, *ibid.* xciv. 215; also Edinb. Phil. Trans. xxi. Pt. 1.)—An alkaloïd existing in opium. It may be obtained by precipitating the aqueous extract of opium with soda; treating the precipitate, which consists for the most part of morphine, with alcohol; evaporating the brown tincture; treating the residue with a dilute acid; and precipitating the filtered solution with ammonia. A brown resinous matter is thereby thrown down, containing a considerable quantity of papaverine; and on dissolving this resin in dilute hydrochloric acid, adding acetate of potassium, which precipitates a dark coloured resin, washing this precipitate with water, treating it with boiling ether and leaving the ethereal extract to cool, papaverine separates in the crystalline form. (**Merck.**)

A simpler method is to dry the resin precipitated by ammonia on the water-bath, and mix it with an equal weight of alcohol, whereby an unctuous mass is formed, which solidifies after a while in a crystalline magma; press this product; recrystallise it from alcohol; and decolorise it with animal charcoal. The papaverine thus obtained still contains narcotine, to separate which it is treated with hydrochloric acid and crystallised, and thereupon the hydrochlorate of papaverine, being sparingly soluble and easily crystallisable, separates, and the whole of the narcotine may be extracted by cold water. (**Merck.**)

Anderson prepares papaverine from the mother-liquor of the preparation of narcotine. (See Opium, p. 209.)

Papaverine crystallises from alcohol in colourless acicular crystals confusedly grouped. It is insoluble in *water*, sparingly soluble in *ether* and *alcohol* at ordinary temperatures, more readily with the aid of heat. The solutions blue reddened litmus paper. It is particularly characterised by assuming a deep blue colour when strong sulphuric acid is poured upon it. It does not appear to be poisonous; indeed it may be swallowed in considerable quantity without producing any particular effect. Its composition is as follows:—

| *Calculation.* | | | Merck. | | Anderson. | |
|---|---|---|---|---|---|---|
| 20 C | 240 | 70·79 | 70·47 | 70·68 | 70·58 | 70·71 |
| 21 H | 21 | 6·20 | 6·32 | 6·65 | 6·29 | 6·46 |
| N | 14 | 4·13 | 4·75 | | 3·96 | 4·40 |
| 4 O | 64 | 18·88 | | | | |
| $C^{20}H^{21}NO^4$ | 329 | 100·00 | | | | |

When papaverine is boiled for some time with *peroxide of manganese*, sulphuric acid and water, the liquid acquires a brown colour, and after some hours deposits crystalline flakes. (**Merck.**)

*Nitric acid* dissolves papaverine without decomposing it; but on mixing the solution with excess of strong nitric acid, red vapours are evolved, the liquid acquires a deep red colour, and orange-coloured crystals are deposited, consisting of **nitrate of nitropapaverine**, $C^{20}H^{20}(NO^2)NO^4.HNO^3$.

*Bromine-water* added drop by drop to papaverine, forms a precipitate which redissolves at first, but afterwards becomes permanent: it consists of **hydrobromate of bromopapaverine**, $C^{20}H^{20}BrNO^4.HBr$.

Alcoholic tincture of *iodine* added to an alcoholic solution of papaverine, forms after a while small crystals of an iodide of papaverine, containing $2C^{20}H^{21}NO^4.I^6$; and the mother-liquor yields by evaporation crystals of another iodide containing $2C^{20}H^{21}NO^4.I^{10}$. (Anderson.)

Papaverine heated with four times its weight of *soda-lime* gives off a volatile alkali, probably tritylamine or ethylamine. (Anderson.)

Heated with *iodide of ethyl* in a sealed tube it does not yield an ethyleted base, but merely hydriodate of papaverine, and apparently alcohol or ether. (How.)

SALTS OF PAPAVERINE.—The *hydrochlorate*, $C^{20}H^{21}NO^4.HCl$, is obtained by dissolving the alkali in dilute hydrochloric acid, and adding an excess of acid; it is then precipitated as an oil which gradually solidifies in large hemihedral crystals belonging to the trimetric system. Observed combination: $\infty P\,.\,\breve{P}\infty\,.\,\frac{P}{2}$. Inclination of the faces, $\infty P : \infty P = 80^\circ$; $\breve{P}\infty : \breve{P}\infty = 129^\circ\,20'$; $\breve{P}\infty : \frac{\breve{P}}{2} = 149^\circ\,15'$.

The *chloroplatinate*, $2C^{20}H^{21}NO^4.H^2Cl^2.Pt^{iv}Cl^4$, is a yellow precipitate insoluble in water and in alcohol.

The *sulphate* is uncrystallisable. The *nitrate* cannot be prepared with nitric acid, because the least excess tends to form a substitution-compound, as above mentioned; but it is obtained by precipitating nitrate of silver with the hydrochlorate.

**PAPYRIN** or *Vegetable Parchment*.—A tough substance produced by the action of sulphuric acid on unsized paper. (See CELLULOSE, i. 819.)

**PARABANIC ACID.** $C^3H^2N^2O^3 = \left.\begin{matrix}(C^2O^2)''\\(CO)''\\H^2\end{matrix}\right\}N^2$. *Oxalyl-carbamide or Oxalyl-urea. Carbonyl-oxamide.* (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 285.)—An acid formed: 1. By the action of oxidising agents on alloxan (i. 136):

$$C^4H^2N^2O^4 \quad + \quad O \quad = \quad C^3H^2N^2O^3 \quad + \quad CO^2.$$

2. Together with alloxantin, by the spontaneous decomposition of alloxan (Baumert, Pogg. Ann. cx. 93):

$$3C^4H^2N^2O^4 \quad = \quad C^8H^4N^4O^7 \quad + \quad C^3H^2N^2O^3 \quad + \quad CO^2.$$

According to Heintz (Pogg. Ann. cxi. 436) both the alloxantin and the parabanic acid suffer further decomposition, the former gradually taking up oxygen and reproducing alloxanic acid, while the latter is first converted, by assumption of water, into oxaluric acid, and then into oxalic acid and urea, and the urea ultimately into carbonate of ammonium.

3. Together with guanidine and small quantities of xanthine, urea and oxaluric acid, by the action of hypochlorous acid on guanine. (Strecker, ii. 951.)

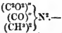
It is usually prepared by dissolving 1 pt. of uric acid in 8 pts. of warm moderately strong nitric acid, evaporating to a syrup and cooling: it then crystallises out, and may be purified by twice recrystallising from water.

Parabanic acid forms thin, transparent, colourless, six-sided prisms, which have a very acid taste, and redden litmus paper (Liebig and Wöhler). The crystals are monoclinic, exhibiting the combination $+P\,.\,-P\,.\,oP\,.\,+P\infty\,.\,-P\infty\,.[\infty P\infty]$. Ratio of principal axis, clinodiagonal and orthodiagonal $= 1 : 0{\cdot}6646 : 0{\cdot}4783$. Angle of the inclined axes $= 81{\cdot}39'$. Angle $-P : -P$ (clinod.) $= 120^\circ\,52'$; $oP : -P\infty = 129^\circ\,18'$; $-P\infty : +P\infty = 113^\circ\,11'$; $oP : +P\infty = 117^\circ\,42'$. Cleavage easy parallel to $[\infty P\infty]$. (Schabus, Jahresb. 1854, p. 470; 1862, p. 359; see also v. Rath, *ibid.* 1860, p. 326.)

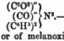
Parabanic acid is easily soluble in *water*, and does not effloresce in the air. When heated to 100° it becomes reddish; at a stronger heat it melts and partly sublimes, partly decomposes, giving off hydrocyanic acid. Its aqueous solution is not decomposed by boiling. When the aqueous solution is boiled with *ammonia* (or other alkalies) it takes up water and is converted into oxaluric acid, $C^3H^4N^2O^4$. With *anhydrous ammonia* parabanic acid appears to form oxaluramide (p. 277); and when heated with *aniline* it forms phenyl-oxaluramide: $C^3H^2N^2O^3 + C^6H^7N = C^9H^9N^3O^3$. (Laurent and Gerhardt.)

The only known salt of parabanic acid is the *silver-salt*, $C^3Ag^2N^2O^3$, which is obtained as a white precipitate when aqueous parabanic acid is added to nitrate of silver (Liebig and Wöhler). The aqueous acid mixed with nitrate of silver and a little ammonia, yields a precipitate containing $2C^3Ag^2N^2O^3.H^2O$, which becomes anhydrous between 130° and 140°. (Strecker.)

*Methyl-parabanic acid*, $C^4H^4N^2O^3 = \left.\begin{matrix}(C^2O^2)''\\(CO)''\\H.CH^3\end{matrix}\right\}N^2$.—This is the compound which Dessaignes obtained by heating the base $C^3H^{10}N^4O^3$ (produced by the action of nitrous acid on creatinine) with hydrochloric acid. It is probably also formed by the action of baryta on creatine at the boiling heat (ii. 102).



*Dimethyl-parabanic acid*, $C^5H^6N^2O^3 = \left.\begin{matrix}(C^2O^2)''\\(CO)''\\(CH^3)^2\end{matrix}\right\}N^2$.—This compound, already described as *cholestrophane* (i. 926), called also *nitrotheine* by Stenhouse, is the final product of the action of chlorine or nitric acid upon caffeine (Rochleder). It may be produced directly from parabanic acid by heating the dry silver-salt of that acid with iodide of methyl to 100° for twenty-four hours. It crystallises from hot water in laminæ having a silvery lustre. (Strecker, Ann. Ch. Pharm. cxviii. 151; Jahresb. 1861, p. 528.)



*Diphenyl-parabanic acid*, $C^{15}H^{10}N^2O^3 = \left.\begin{matrix}(C^2O^2)''\\(CO)''\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Produced by treating a boiling alcoholic solution of dicyanomelaniline or of melanoximide (p. 286) with an aqueous acid:

$$\underset{\text{Dicyanomelaniline.}}{C^{15}H^{13}N^5} + 3H^2O + 3HCl = \underset{\text{Diphenyl-parabanic acid.}}{C^{15}H^{10}N^2O^3} + 3NH^4Cl;$$

$$\underset{\text{Melanoximide.}}{C^{15}H^{11}N^3O^2} + H^2O + HCl = C^{15}H^{10}N^2O^3 + NH^4Cl.$$

Diphenyl-parabanic acid crystallises in needles, is insoluble in water, but easily soluble in alcohol and in ether. By boiling with potash it is resolved into carbonic acid, oxalic acid and phenylamine. (Hofmann, Proc. Roy. Soc. xi. 275.)

Cyanamide forms with 2 at. cyanogen a yellow amorphous body, $C^3H^2N^4$ (= $NH^2(CN) + C^2N^2$), analogous to dicyanomelaniline, and it might have been expected that this body when heated with aqueous acids would yield parabanic acid by a reaction similar to the above, namely:

$$C^3H^2N^4 + 3H^2O + HCl = C^3H^2N^2O^3 + 2NH^4Cl;$$

but the product actually obtained is altogether different. (Hofmann.)

**PARABENZENE** or *Parabenzol*. (Church, Phil. Mag. [4] xiii. 415; xviii. 522.)—A hydrocarbon isomeric with benzene (i. 541), occurring, together with the latter and its homologues, in light coal-tar oil. When purified by rectification it boils at 97·5° (benzene at 80·4°, Kopp); does not solidify at −20° (benzene solidifies at 0°); has a faint alliaceous odour, less pleasant than that of pure benzene. Treated with nitric acid of specific gravity 1·5, it yields a nitro-compound which appears to be identical with ordinary nitrobenzene; and with a mixture of strong nitric and sulphuric acids, a dinitro-compound, agreeing in composition and properties with dinitrobenzene. Treated with 4 vols. of fuming sulphuric acid, it forms a sulpho-acid isomeric but not identical with sulpho-benzolic acid, inasmuch as its *barium-salt*, $C^{12}H^{10}Ba''S^2O^6$, is obtained only as a gummy mass exhibiting no trace of crystallisation, insoluble in ether, very slightly soluble in alcohol; the *copper-salt*, $C^{12}H^{10}Cu''S^2O^6$ (at 100°), is a very soluble, translucent, amorphous bluish mass; and the free acid separated from the salt by sulphuretted hydrogen crystallises with difficulty in prisms which are but slightly deliquescent; whereas the barium-salt of ordinary sulpho-benzolic acid crystallises in nacreous laminæ; the copper-salt in crystals which are less soluble in water than the isomeric salt, and become anhydrous only at 170°; and the free acid forms deliquescent crystals. The *ammonium-salt* of parasulpho-benzolic acid when subjected to distillation yields parabenzene with all the properties above mentioned.

**PARABROMALIDE.** $C^2HBr^3O$.—A compound isomeric with bromal (i. 666), produced by gradually adding bromine to wood-spirit contained in a retort, through a funnel tube reaching to the bottom of the liquid. Two layers of liquid then collect in the receiver, the upper consisting of aqueous hydrobromic acid, while the lower, which is oily, solidifies, after washing with water and exposure to the air, to a mass of colourless crystals of parabromalide, which, when purified by pressure between paper and recrystallisation from strong alcohol, forms colourless rhombic prisms with four-sided summits. It has a specific gravity of 3·107, melts at 67°, begins to decompose at 200° with separation of bromine and hydrobromic acid, and decomposes completely at a higher temperature, leaving a copious residue of charcoal. It is insoluble in *water*, soluble in strong *alcohol* and in *chloroform*. By dilute *potash* it is decomposed, like bromal, yielding bromoform and acetate of potassium. *Alcoholic ammonia* acts upon it in a similar manner, but when heated with it to 100° in a sealed tube, gives rise to a more complicated reaction, the liquid containing, besides formate of ammonium, the products of the action of alcoholic ammonia on bromoform, and a brown powder, probably impure cyanhydrin. (Cloez, Ann. Ch. Pharm. cxi. 178.)

**PARABROMOMALEIC ACID.** See MALEIC ACID (iii. 788).

**PARACACODYLIC OXIDE.** See OXIDE OF CACODYL, under ARSENIC-RADICLES, ORGANIC (i. 407).

**PARACAJPUTENE.** See CAJPUTENE (i. 711).

**PARACAMPHORIC ACID.** Syn. with INACTIVE CAMPHORIC ACID (i. 730).

**PARACARTHAMIN.** This name is given by Stein (Rép. Chim. pure, v. 108; Jahresb. 1862, p. 500; 1863, pp. 561, 596) to a red substance allied to carthamine, produced by the action of sodium-amalgam on rutin. It is turned green by alkalis and by neutral acetate of lead, the red colour being restored by acids. Paracarthamin appears also to be contained in the red bark of dog-wood (*Cornus sanguinea*), in the young bark of certain kinds of acacia, in the blackberry, in the red sterile shoots of *Euphorbia cyparissias*, and in the layer of the willow-stem between the pith and the bark.

**PARACELLULOSE.** Frémy applies this name to that modification of cellulose which does not dissolve in an ammoniacal solution of cupric oxide till it has been subjected to the action of acids, alkalis, or other reagents, restricting the term cellulose to that variety which is immediately soluble in that liquid. Both varieties of cellulose are soluble in boiling potash-ley. The utricular tissue forming the medullary rays of wood consists of paracellulose. Frémy regards these modifications of cellulose as essentially distinct. Payen, on the other hand, is of opinion that there is but one kind of cellulose, chemically speaking, and that the differences observed in the reactions of cellulose from different sources are due to differences of aggregation, or to the presence of inorganic substances. [See Frémy, Compt. rend. xlviii. 202, 275, 325, 362, 862; xlix. 561; Rép. Chim. pure, i. 270, 357, 433, 602; J. Pharm. [3] xxvi. 5.—Payen, Compt. rend. xlviii. 319, 328, 772, 893; Rép. Chim. pure, i. 269, 359, 434; also Jahresb. 1859, pp. 529, 541.]

**PARACETONE.** See PINACONE.

**PARACHLORALIDE.** $C^2HCl^3O^2$.—A substance isomeric with chloral (i. 880), produced by the action of chlorine on pure anhydrous wood-spirit in diffused day-light. The containing vessel should be cooled at first, but to complete the reaction a gentle heat is required, so that the product may distil over in an atmosphere of chlorine. The oily portion of the distillate is then to be mixed with an equal volume of strong sulphuric acid, and after 24 hours' contact, distilled from oxide of lead in an atmosphere of carbonic anhydride.

Parachloralide is a pungent-smelling liquid resembling chloral. Specific gravity 1·5765 at 14°. Boils at 182°, and volatilises almost without residue. It is distinguished from chloral by its insolubility in water, and its higher boiling point (chloral boils at 98·6°, Kopp). With fixed alkalis and alcoholic ammonia, it reacts like parabromalide. (Cloez, Ann. Ch. Pharm. cxi. 178; Jahresb. 1859, p. 434.)

**PARACHLOROBENZOIC ACID.** $C^7H^5ClO^2$. *Chlorodracylic acid* (Wilbrand and Beilstein, Ann. Ch. Pharm. cxxviii. 257; Beilstein and Schlun, *ibid.* cxxxiii. 242).—An acid isomeric with chlorobenzoic acid, produced, together with hydrochlorate of paraoxybenzamic acid, by the action of hydrochloric acid on azo-paraoxybenzamic acid (p. 352). It is a crystalline body, which melts at 236°—237°, and sublimes in scales resembling naphthalene, at a temperature very near its melting point. Normal chlorobenzoic acid, obtained from benzoic acid or its derivatives, or from hippuric or cinnamic acid (compounds capable of yielding benzoic acid), melts at 152° or 153°, and sublimes in needles; chlorosalylic acid (called parachlorobenzoic acid at page 555, vol. i.), produced by the action of pentachloride of phosphorus on salicylic acid, melts at 137° and forms a calcium-salt containing 2 at. water ($C^{14}H^{12}Ca''O^4.2H^2O$), whereas the calcium-salt of the parachlorobenzoic acid just described contains 3 at. water, like that of normal chlorobenzoic acid.

**PARACITRIC ACID.** Syn. with ACONITIC ACID.

**PARACOLUMBITE.** A mineral found at Taunton, Massachusetts, in black grains, which melt easily before the blowpipe to a black glass, form a yellow-brown glass with borax, and are decomposed by sulphuric acid, with evolution of hydrofluoric acid and separation of a white powder. The mineral is said to contain iron and uranium, but no titanium. (Shephard, Sill. Am. J. ii. xii. 209; *Dana's Mineralogy*, ii. 501.)

**PARACYANIC ACID.** This name is applied to several brown products, of uncertain composition, resulting from the decomposition of cyanogen or some of its compounds, in presence of water. They are partially soluble in water, and when heated give off hydrocyanic acid and ammonia, leaving a mixture of charcoal and paracyanogen.

**PARACYANOGEN.** A brown or black substance isomeric or polymeric with cyanogen, which remains in small quantity when the latter is prepared by heating cyanide of mercury (ii. 275). To obtain it pure, however, it is necessary to use perfectly dry cyanide of mercury, since, if moisture is present, a certain quantity of ammonia is produced, and the paracyanogen is contaminated with free carbon.

When pure paracyanogen is calcined in a gas which does not act upon it, such as nitrogen or carbonic anhydride, it is completely converted into cyanogen, without leaving any carbonaceous residue. Paracyanogen heated in a current of chlorine, gives off a considerable quantity of white fumes having a suffocating odour, which condense on the cold parts of the apparatus in the form of a white sublimate soluble in water.

When cyanide of silver is gently heated, it melts without decomposing; but on raising the temperature, cyanogen is given off, and at a certain moment, the evolution of gas becomes violent, and the whole mass exhibits incandescence. A light grey residue is then obtained, possessing the metallic lustre and amounting to 90 per cent. of the original salt. This residue is not pure silver, inasmuch as it still gives off cyanogen at a higher temperature, and dilute nitric acid extracts silver from it, leaving a brown substance still containing 40 per cent. of silver.

According to Thaulow (J. pr. Chem. xxxi. 226), cyanide of silver when heated gives off only half its cyanogen (1 grm. yielding from 48 to 50 cub. cent. of the gas). The residue partly amalgamates with mercury, whence it appears to be a mixture of metallic silver and *paracyanide of silver.* (For further details, see *Gmelin's Handbook*, xi. 371.)

**PARADIGITALETIN.** $C^{22}H^{34}O^{7}$.—A product of the decomposition of digitalosin by dilute sulphuric acid (ii. 330).

**PARADIPHOSPHONIUM-COMPOUNDS.** See PHOSPHORUS-BASES.

**PARA-ELLAGIC ACID.** Syn. with RUFIGALLIC ACID.

**PARAFFIN.** The colourless, crystalline, fatty substance known by this name is the solid portion of the mixture of oily hydrocarbons produced, together with a variety of other substances, in the dry or destructive distillation of various organic bodies, and of bituminous minerals, at temperatures not exceeding a low red heat. It also occurs as a constituent of many varieties of petroleum or mineral oil, associated with liquid hydrocarbons similar to, if not identical with, those contained in the tar produced by destructive distillation. Native paraffin in a solid state occurs also in the coal measures and other bituminous strata, constituting the minerals known as fossil-wax, hatchettin, ozocerite, &c. As a product of destructive distillation, it was discovered in 1830 by Reichenbach, who obtained it first from wood-tar; then from animal tar, and lastly from coal-tar made by distillation at a temperature below full red heat. As a constituent of petroleum it was discovered about the same time by Christison, who obtained it from Rangoon petroleum, and described it under the name of *petroline*. Ettling also obtained it by distilling wax with lime, and in 1833 Laurent obtained it, together with liquid hydrocarbons, by distilling bituminous shale at a temperature not exceeding a low red heat. It has since been extracted abundantly both from the tar obtained by distilling coal, bituminous shale, lignite, and peat, at a moderate heat, as well as from many varieties of petroleum or mineral oil, and its preparation now forms a part of one of the most extensive and important branches of manufacturing industry.

The substance known as paraffin does not possess any chemical individuality, but is more probably a mixture of several hydrocarbons, just in the same manner that the liquid oil generally associated with paraffin in petroleum, and always produced together with it in destructive distillation below full red heat, is a mixture of several homologous hydrocarbons. (See PETROLEUM.)

The paraffin of commerce, when pure, is a solid, colourless, translucent substance, perfectly inodorous and tasteless, somewhat resembling spermaceti. It has a density of about 0·870; melts at from 45° to 65° C., forming a colourless oil, which solidifies to a lamino-crystalline mass. It boils about 370°, and, when cautiously heated, volatilises without much decomposition. It does not absorb oxygen from the air at ordinary temperatures, does not burn easily in the mass, but from a wick it burns with a very bright flame. It is insoluble in water, soluble in 2·85 pts. of boiling *alcohol*, but separates completely on cooling in snow-white needles, which are soft, friable, and greasy to the touch. It is much more soluble in *ether* and in *oils*. It is but slowly attacked by strong *sulphuric acid* even at temperatures above 100°, not at all by dilute *nitric acid;* but, when heated for some time with strong *nitric acid*, it is stated to yield succinic acid together with a small quantity of butyric acid. *Chlorine* does not act upon it at ordinary temperatures, but, according to Bolley (Ann. Ch. Pharm. cvi. 230), chlorine passed into melted paraffin attacks it slowly, forming a hard but easily fusible substitution-product, which he calls *chloraffin*. Altogether paraffin is a very stable and indifferent substance: hence its name (from *parum affinis*).

The production of paraffin and of the liquid hydrocarbons—known by the names of *eupione*, *photogen*, *paraffin oil*, &c.—which accompany it in the tar or oily product of destructive distillation, was shown by Reichenbach to be a constant result of carbonisation, or the decomposing action of heat upon all organic substances and minerals of organic origin, such as coal, &c. (Journ. f. Ch. Phys. lx. 280). He also showed that, in order to obtain the largest possible amount of these products from any particular material, the most essential condition was the limitation of the temperature within such a degree that the vapour of the products resulting from carbonisation should not suffer further decomposition of such a nature as to give rise to the production of a large amount of permanent gas, naphthalene, soot, &c. (Journ. f. Ch. Phys. lxi. 182). The extreme limit of temperature to be applied in the destructive distillation of coal, &c., for the purpose of obtaining paraffin and the oily products allied to it, was ascertained by him to be incipient redness, or a low red heat, beyond which temperature he showed that a secondary decomposition of those products of true carbonisation took place (*ibid.* lxiii. 229). Consequently he pointed out that the precautions to be observed in conducting destructive distillation, with the object of producing paraffin and those oils, consisted in raising the heat gradually, and never allowing the sides of the retort to attain a red heat (*ibid.* lxi. 178, lxviii. 229).

The amount of paraffin contained in the tar produced by destructive distillation below a full red heat, is always very small in proportion to the liquid hydrocarbons mixed with it. These latter often constitute from 70 to 80 per cent. of the crude tar by weight, while the paraffin rarely amounts to 5 per cent., and more frequently to only 1 or 2 per cent., according to the material distilled. This crude tar also contains a pitchy oil heavier than water, together with carbolic acid and its homologues, picoline, and other basic oils, &c. The amounts of these several constituents, and of hydrocarbons contained in such tar, vary very considerably according to the material from which it is obtained, and determine its value for the purpose of the refiner. The physical characters of such tar also differ, according to the proportions of these constituents; sometimes it is quite solid—peat-tar—more generally it is liquid at the ordinary temperature, or at most thick—shale-tar, coal-tar. Its specific gravity varies from upwards of 0·900 to 0·840.

The tar thus obtained from shale or coal differs essentially in every respect from the tar obtained in the ordinary process of gas making, in which the coal is subjected to a bright red heat, though some kinds of tar from gas-works, in which the richer cannel coals are used, not unfrequently contain paraffin and probably some paraffin oil, which have escaped decomposition by reason of the abundance of volatile products given off. In such tar, however, these substances are always mixed with naphthalene, homologues of benzol, pitch, &c., so that they cannot be conveniently separated from these latter and purified. (See TAR.)

The composition of paraffin from several sources is shown in the following table: *a.* From Boghead coal; melting at 45·5°, and solidifying after fusion in a crystalline mass.—*b.* From the same; melting at 52°, solidifying in a granular mass.—*c.* From Rangoon tar; melting at 61°.—*d.* From peat; melting at 46·7°.—*e.* From Chinese wax, *cerotene* (i. 836); melting at 57° or 58°.—*f.* From beeswax, *melene* (iii. 868); melting at 62°.

| | Anderson * | | | | | Brodie.† | | |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | | *e.* | | *f.* |
| Carbon | 85·1 | 85·0 to 85·3 | 85·15 | 84·95 | 85·23 | 84·60 | 85·20 | 85·31 |
| Hydrogen | 15·1 to 15·3 | 15·4 | 15·29 | 15·05 | 15·16 | 14·39 | 14·23 | 14·44 |

Paraffin has been usually regarded as an olefine or mixture of olefines of high atomic weight; but the formula of these bodies $C^nH^{2n}$ requires 85·71 per cent. carbon, which is considerably above that in most of the preceding analyses. The analytical results are in fact more nearly represented by the formula of one of the higher homologues of marsh-gas, $C^{27}H^{56}$, for example, requiring 85·2 per cent. carbon, which agrees exactly with the second of Brodie's analyses of cerotene or Chinese wax paraffin, and $C^{30}H^{62}$ requiring 85·3 per cent. carbon, which agrees with the analysis of melene or the paraffin of common bees-wax. Hence it is more probable that paraffin is a homologue or mixture of several homologues of marsh-gas of high atomic weight. This view of its constitution is also in accordance with its chemical indifference, the alcoholic hydrides $C^nH^{2n+2}$ being especially characterised by the feebleness of their combining tendencies. These hydrides when treated with chlorine do not unite with it like the olefines, but yield substitution-products, which is likewise the case with the paraffin examined by Bolley (*vid. sup.*) and with Brodie's cerotene and melene. Moreover, paraffin appears to be closely related to the hydrocarbons $C^nH^{2n+2}$ in its mode of formation; it is associated with these bodies in petroleum, especially in that of Pennsylvania, which has been shown to contain the whole series from marsh-gas up to solid hydrocarbons (paraffins) of very high atomic weight (iii. 181); and in the decomposition of coal, &c., the condition most favourable to the production of paraffin, namely, distillation at a comparatively low temperature, is likewise that which yields the hydrides of ethyl, amyl, &c., in largest quantity. For all these reasons it is most probable that paraffin is an alcoholic hydride or a mixture of several alcoholic hydrides of the marsh-gas series $C^nH^{2n+2}$.*

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* Rep. Brit. Assoc. 1846. Notices and Abstracts, p. 49; Jahresb. 1857, p. 480.

† Phil. Mag. [3] xxxiii. 178.

Paraffin is susceptible of several useful applications. As it burns with a bright flame, and is very hard when its melting point is above 45° C., it makes excellent candles. It is also largely used as a substitute for sulphur for dipping matches, and Dr. Stenhouse has patented its application to woollen cloths to increase their strength and make them waterproof.† More extensive however are the uses of the oils produced simultaneously with solid paraffin by the distillation of coal, &c., at low temperatures, and existing with it in petroleum. These oils, doubtless consisting in great part of members of the paraffin or marsh-gas series, differ greatly in density and boiling point, as met with in commerce under the names of eupione, photogen, paraffin oil, solar oil, &c.; some of them hold paraffin in solution and deposit it at low temperatures. They are extensively used for burning in lamps, and to some extent for lubricating machinery.

The more volatile of these oils having a density of 0·800 to 0·830 are peculiarly well adapted for artificial illumination, as they consist of hydrocarbons free from oxygen, and therefore produce flame rich in incandescent carbon. Hence with a properly regulated supply of air, these oils produce a more brilliant light than that obtained by the consumption of an equal amount of animal or vegetal oils which generally contain a considerable amount of oxygen.

The least volatile of these oils which have a density above 0·860 would be safer than many of the fat oils in use for lubricating, inasmuch as they do not absorb oxygen, and consequently cannot endergo spontaneous combustion when smeared on cotton waste; but unfortunately these oils generally possess but little body, and are therefore far less efficient lubricants than fat oils, so that they can only be used when mixed with the latter. In this way however they are very serviceable in rendering fat oils, like rape and cotton-seed oils, which become gummy by exposure to air, more suitable for use as lubricants than they would be alone. The presence of paraffin dissolved in these hydrocarbon oils has been erroneously stated to render them good lubricants; but that is not the case, in fact the presence of paraffin is rather a disadvantage than otherwise, since the oils containing it are liable to solidify on the journals of machinery at temperatures little below 60° F.

### *Preparation of paraffin.*

1. From *wood-tar.*—Reichenbach extracted paraffin from wood-tar by distilling it and collecting apart the denser portion of the oil which passed over towards the end of the operation, redistilling this and collecting the distillate in separate fractions. On cooling the least volatile portion of this distillate, paraffin crystallised out in scales which could be separated by filtration and freed from adhering oil by pressure between folds of unsized paper. Or this portion of the distillate was shaken with six or eight times its bulk of alcohol (36° Beaume, 85 per cent.) whereby the liquid oil was dissolved and a thick mass of paraffin scales precipitated, which were collected on a filter-cloth, washed with alcohol until almost colourless, and then crystallised from solution in boiling alcohol. (Journ. f. Ch. Phys. lix. 437.)

2. From *coal-tar*, in the production of which the necessary precautions as to temperature and gradual heating had been observed, Reichenbach extracted paraffin by distilling the crude coal-tar, and collecting the thick oil constituting the second half of the distillate, apart from the more volatile thin liquid oil forming the first half of the distillate. By exposing this least volatile portion of the coal-tar oil to a winter temperature, paraffin crystallised out in laminæ, and after separating a further portion of oil by another fractional distillation, solid paraffin was obtained by treating the thick honey-like portion distilling over last with alcohol as above described. To purify this paraffin it was agitated for a time with about twice its bulk of concentrated sulphuric acid at from 90° to 100° C., after which the paraffin separated on the surface as a colour-

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* The word "paraffin" might be conveniently used as a generic name for the hydrocarbons of this series, marsh-gas being called *methylic paraffin*; hydride of ethyl, *ethylic paraffin*; Brodie's cerotene, *cerotic paraffin*, &c.

† Specifications, 1862, Nos. 55 and 180.

less liquid which solidified on cooling. This, after crystallisation from alcohol, was considered by Reichenbach to be pure paraffin, so far as the state of chemistry at that time permitted him to judge (Journ. f. Ch. Phys. lxi. 274–277, 279). A more easy method of extracting paraffin recommended by Reichenbach consisted in separating the liquid oil and concentrating the paraffin as far as possible by repeated fractional distillation, then shaking the semi-solid mixture of oil and paraffin with from one fourth to one half its bulk of concentrated sulphuric acid, added in successive small portions, and digesting this mixture at 50° C. until paraffin separated on the surface, or else distilling it. (Journ. f. Ch. Phys. lxi. 283–287.)

*Manufacture of Paraffin Oil and Paraffin.*—Although the application of oily products of destructive distillation for lighting, lubricating and other purposes had been attempted and to some extent practised long before the discovery of paraffin and Reichenbach's elucidation of the conditions essential for the production of these substances, still it was not until after this period that their manufacture was prosecuted with any kind of scientific basis. Very soon after that, however, attempts were made to introduce these products into commerce, and to apply them to the purposes for which they were so evidently suited. The chief desideratum was a material which was capable of yielding a sufficient amount of oil, &c., to be worked remuneratively. The materials which have chiefly been employed or tried for this purpose are the following.

1. *Bituminous shale.*—The first step in the industrial application of Reichenbach's results was made in 1830 by Aug. Laurent, who suggested the working of the bituminous shale in the Autun coal-measures as a source of paraffin and oil for burning in lamps. This shale yielded, when gradually heated to a low red heat, about twenty or twenty-five gallons of tar or crude paraffin oil per ton, containing a small amount of solid paraffin. By fractional distillation the tar was separable into light burning oil, thick oil for lubricating, paraffin and pitchy residuum, and these several products were purified by successive treatment with sulphuric acid and caustic soda. Several works were established in that district, and at the Paris Industrial Exhibition in 1839, the products manufactured there by Selligne were shown, viz.: 1. Crude oil or shale-tar. 2. Volatile spirit. 3. Oil for burning in lamps. 4. Grease for machinery. 5. Tar-grease. 6. Paraffin crystallised, and paraffin candles. This manufacture, though it has been continued more or less up to the present time, did not attain any great importance, partly from the want of efficient methods of purifying the oil, and of suitable lamps for burning it, partly also from the remote situation of Autun, and the small amount of oil which the shale was capable of yielding. Since then bituminous shale has been worked at other places, as for instance at Wareham in Dorsetshire; but the small amount of produce has always been an obstacle, especially while richer materials, to be mentioned presently, were worked under special advantages, and while the copious supply of petroleum from America continued. But now that these conditions are changed, bituminous shale yielding about the same average produce as the Autun shale is being worked with considerable advantage in Scotland.

2. *Petroleum*, which generally contains paraffin-oil and paraffin ready formed as constituents of it, was the first material which was successfully worked for the manufacture of hydrocarbon oil, chiefly for lubricating and to some extent for burning. About the year 1847, Mr. James Young, then of Manchester, obtained the right of working a spring of dense petroleum (specific gravity 0·900) which had been discovered in a Derbyshire coal mine, and he succeeded in rendering it available during a period of two or three years. In 1854 a patent (No. 2,719) was granted to Mr. Warren De La Rue for the manufacture of paraffin and other hydrocarbons from petroleum. The raw material which he used was the Rangoon tar already described (p. 3). This substance is submitted to a current of steam in a capacious still which can also be heated externally. The more volatile portion then distils over, and is afterwards separated by rectification in a similar apparatus into products differing in volatility. The last portions of the residue are then raised to a higher point, while superheated steam is passed through it. The last portions of this second distillate are very rich in paraffin, which is separated as far as possible by cooling and filtration. It is then submitted to pressure, and is finally purified by admixture with sulphuric acid at 100° C., washing with soda-ley, and distillation. The heavy oils separated from the paraffin are said to be well adapted for lubrication. The proportion of the several products obtainable in this manner from Rangoon tar has been already given under NAPHTHA (p. 3). This Rangoon petroleum was largely worked until about the year 1860, when enormous quantities of petroleum began to be imported from America, and for a time almost superseded every other source of supply (see PETROLEUM). These supplies are now rapidly decreasing.

4. *Peat.*—About 1849 an attempt was made on a large scale in Ireland to obtain paraffin-oil and paraffin by the distillation of peat, but the yield of crude oil, not more than two gallons per ton, was too small to be remunerative. Certain kinds of peat have however been worked successfully on the Continent and in the Hebrides. At the latter

place as much as five to ten gallons of refined oils and paraffin were obtained from the ton of peat. A serious obstacle to the working of this material is the strong disagreeable smell of the oil obtained.

4. *Lignite.*—This material has been largely used on the Continent for the manufacture of paraffin-oil and paraffin. About the year 1850 works were established at Beul opposite Bonn on the Rhine, and at Weissenfels (p. 344). The process is fully described in Hofmann's Report on Chemical Products and Processes in the International Exhibition of 1862. The products obtained in the final rectification are: *a.* Volatile oils called photogen, and solar oils used for illuminating; *b.* Paraffin; *c.* A volatile spirit called benzol;[*] *d. Phenol* or *Carbolic acid* obtained as a bye-product by treating the oils with caustic soda in their purification, and neutralising the alkaline liquor with sulphuric acid.

The liquid called "photogen" is a volatile oil, which, in properly constructed lamps, gives a light equal to that of gas, and burns very economically. The first quality has a specific gravity of 0·785 to 0·795, and is as clear as water. The second quality is rather yellow, and has a specific gravity of 0·805. The third quality, called "solar oil," is yellow, has a specific gravity of 0·835, and is used for the illumination of rooms, streets, railway carriages, and locomotives.

The purification of the crude paraffin, separated by refrigeration from the paraffin oil, is commenced by placing it in centrifugal machines, by which a further quantity of thick oil is expelled. The mass thus obtained is then cast into cakes, and submitted to hydraulic pressure, first in the cold, afterwards with application of a gentle heat. The object of this last operation is to remove all hydrocarbons having a lower melting point than 40° C. (104° F.). For this purpose there are placed on the horizontal presses between each pair of paraffin cakes, hollow plates through which water of 35°—40° C. (95°—104° F.), is made to flow. In this way the hydrocarbons in question are fused and squeezed out. The pressed paraffin is then heated to 150° C. (302° F.), either over a fire or by means of steam, and the melted mass is mixed with 2 per cent. of strong sulphuric acid, by means of which all the hydrocarbons, not being paraffin, are carbonised, while the pure paraffin remains unaltered. The latter is then carefully washed with hot water, and mixed after cooling with the best colourless photogen, and introduced into iron jacket-cylinders, in which it can be kept warm, and where it is filtered through animal charcoal. The paraffin is thus rendered white, and may be completely separated from photogen by treatment with slightly superheated steam. The paraffin thus obtained is perfectly colourless, and beautifully translucent; it melts at 60° C. (140° F.), and is so hard that candles made of it are said not to bend when exposed to a temperature of 30° C. (86° F.).

5. *Coal.*—The coal from which Reichenbach obtained paraffin oil and paraffin was the kind commonly used as fuel and capable of yielding only a small amount of tar by distillation at a low red heat, probably not more than ten gallons from the ton. For this reason alone it would have been impossible to employ such a material as a source of these products, especially at that time. Varieties of coal and similar minerals have however been discovered since then, some of which are capable of yielding as much as 100 gallons of crude tar per ton. A mineral of this kind, somewhat approximating to coal, or rather intermediate between bituminous shale and what was commonly known as coal, occurs near Bathgate in Scotland, and was being introduced for gas-making under the name of Boghead gas coal or Cannel coal, just about the time when the stoppage of the petroleum spring above mentioned compelled Mr. Young to seek another source of supply for the manufacture of lubricating and burning oil. After having made many trials of different kinds of coal which did not yield by distillation a sufficient amount of oily products to be worked advantageously, or a tar of such a character as is suitable for this purpose, Mr. Young fortunately became acquainted with the Boghead or Torbanehill mineral in 1850, and finding it to yield by distillation an unusually large amount of paraffin-oil, he at once obtained a patent (No. 13,292) for a method of "treating bituminous coals to obtain paraffin and oil containing paraffin therefrom," which consisted in distilling them in an iron retort "gradually heated up to a low red heat," and kept at that temperature until volatile products ceased to come off. Under the protection of this patent he has since developed this manufacture into a highly important branch of industry. Owing to the exceptional richness of the Boghead mineral as a source of paraffin oil, it was for a long time impossible to compete with it by working bituminous shale yielding only about twenty gallons of crude tar per ton, although that material was not comprised under the patent, and up to the year 1860 no other material was known which could be used for this purpose with the same advantage as the Boghead mineral. Consequently it was the only material used until the Leeswood cannel was discovered near Mold in Flintshire, a true cannel coal which yields nearly

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[*] The liquid known by this name is not the benzol obtained from gas-tar naphtha, but a mixture of the lower hydrides homologous with marsh-gas or that portion of the oil which is too volatile for burning in lamps with safety.

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as much oil as the Boghead mineral, and which has since been largely worked for the production of paraffin oil and paraffin.

In the manufacture of these products by the distillation of coal, &c., it is very important, for the reasons above stated, to prevent the heat from rising above low redness, since at higher temperatures a considerable portion of the liquid products are converted into permanent gas.

The following is a list of the principal memoirs relating to paraffin and allied matters, arranged chronologically:—

1830. Reichenbach.—Preparation of paraffin by the dry distillation of wood; its properties. *Schw. J.* lix. 436; lxi. 273; lxii. 129.

1832. Ettling.—Formation of paraffin by the dry distillation of wax. *Ann. Ch. Pharm.* ii. 253.

1835. Laurent.—Occurrence of paraffin in the products of the distillation of bituminous shale. *Ann. Ch. Pharm.* xvi. 273.

1848, 1850. Brodie.—Paraffin from beeswax and Chinese wax. *Ann. Ch. Pharm.* lxvii. 210; lxxvi. 156.

1849. Reece.—Preparation of paraffin by the dry distillation of peat. *Times*, July 28, 1849; *Dingl. pol. J.* cxiii. 237, 317.

1850. James Young.—Specification of patent for treating bituminous coals, to obtain paraffin and oil containing paraffin therefrom (No. 13,292).

1851. Kane, Sullivan and Gages.—The nature and products of the process of the destructive distillation of peat. Museum of Irish Industry; *Report to Chief Commissioner of Woods.*

1852. Reichenbach.—Purification of crude paraffin by distillation with sulphuric acid. *Jahrbuch d. k. k. geolog. Reichsanstalt*, iii. No. 2, p. 36.

1853. W. Brown.—Preparation of volatile products, especially paraffin, from coals and bituminous substances. *Chem. Gaz.* 1853, p. 476.

1854. Warren De La Rue.—Specification of patent for the manufacture of paraffin and hydrocarbons from petroleum (No. 2,719).

1855. Wagenmann.—Manufacture of paraffin and volatile hydrocarbons from coal and bituminous shale. *Dingl. pol. J.* cxxxvii. 36.

1855. Angerstein.—Preparation of similar products from inferior kinds of lignite or peat. *Dingl. pol. J.* cxxxvii. 49.

1855. Fresenius.—Examination of certain lignites from the Westerwald, with respect to the products which they yield by dry distillation. *Dingl. pol. J.* cxxxviii. 129.

1855. Engelbach.—Products of the distillation of bituminous shale from Werther, near Bielefeld. *Dingl. pol. J.* cxxxviii. 380.

1855. H. Schröder.—Products of the distillation of the bituminous shale of Bruchsal. *Dingl. pol. J.* cxxxviii. 437.

1855. Karmarsch.—Illuminating power and value of paraffin-candles. *Dingl. pol. J.* cxxxviii. 188.

1856. H. Vohl.—On the products of the distillation of Rhenish shale (*Blätterschiefer*), various kinds of lignite and peat. *Ann. Ch. Pharm.* xcvii. 9; xcviii. 181.—*Dingl. pol. J.* cxxxix. 216; cxl. 63.—*J. pr. Chem.* lxvii. 418; lxviii. 504.—*Chem. Centr.* 1856, pp. 342, 455.

1856. C. Müller.—Products of the distillation of lignite from the neighbourhood of Aussig in Bohemia. *Zeitschr. Pharm.* 1856, p. 90.

1856. P. Wagenmann.—On the amount of paraffin, &c., obtained from various kinds of peat, lignite, and shale (p. 345). *Dingl. pol. J.* cxxxix. 293.—On the preparation of photogen and paraffin from peat and lignite by distillation in furnaces. *Dingl. pol. J.* cxl. 461; *Chem. Centr.* 1856, p. 699.—On paraffin and photogen in general. *Dingl. pol. J.* cxxxix. 302.—On the distillation of paraffin oil and photogen in vacuo. *Dingl. pol. J.* cxxxix. 43; *Chem. Centr.* 1856, p. 97.

1856. Bellford.—Apparatus for obtaining paraffin and mineral oil from shale and other bituminous substances. *Repertory of Patent Inventions*, Aug. 1856; *Dingl. pol. J.* cxxxix. 42.

1857. Process (patented in the name of A. V. Newton) for obtaining oil adapted for illumination, from lignite and bituminous shale, by the first distillation. *Repertory of Patent Inventions*, Jan. 1857; *Dingl. pol. J.* cxxxix. 42.

1857. Vohl.—On the preparation and purification of solid and liquid distilled products adapted for illumination, from mineral substances. *Ann. Ch. Pharm.* ciii. 283.—On the quantities of photogen, paraffin, &c., obtained from the lignite of the Rhön. *Dingl. pol. J.* cxliii. 363; from the peat of Rostockina in Russia, *ibid.* cxliv. 444; and from the Posidonienschiefer of Wurtemburg, *ibid.* cxlv. 47.—Report on the quantities of volatile illuminating materials obtainable from various bituminous materials, *ibid.* cxlv. 51.—Similar reports by P. Wagenmann, *ibid.* cxlv. 309; and C. Müller, *ibid.* cxlvi. 210.

1857. B. Hübner and R. Körkel.—On the quantities of light and heavy oils, paraffin, &c., obtainable from various kinds of coal. *Dingl. pol. J.* cxliii. 143; *Chem. Centr.* 1857, p. 130.

1857. Tb. Engelbach.—General view of the products of the distillation of mineral substances, &c., as illuminating materials, and especially the bituminous sand of Heide in Holstein. *Ann. Ch. Pharm.* ciii. 1.

1857. B. Hübner.—On the industrial working of lignites for the preparation of photogen, paraffin, &c. *Dingl. pol. J.* cxlvi. 211, 418.

1857. Orth.—Illuminating power of schist-oils. *Dingl. pol. J.* cxliv. 398.

1858. Vohl.—Further communications respecting the preparation of paraffin, and the utilisation of the secondary products obtained in its manufacture. *Ann. Ch. Pharm.* cvii. 45.—In abstract, together with the results of previous communications. *J. pr. Chem.* lxxv. 289; *Rép. Chim. app.* i. 37.

1858. C. Sprengel. L. Unger.—On the dry distillation of lignite and other bituminous minerals. *Dingl. pol. J.* cxlix. 220, 458; cl. 130.

1858. Vohl.—Examination of Burmese naphtha or Rangoon tar as a raw material for the preparation of photogen and paraffin. *Dingl. pol. J.* cxlvii. 374.—J. Barlow. On the treatment of this mineral oil for obtaining a paraffin-like substance (*Belmontin*), liquid hydrocarbons fit for illumination, &c. *Cosmos,* xii. 513.

1858. Vohl.—On two illuminating materials, viz. *Pinolin* (a product of the distillation of American pine-resin), and *Oleone* (a product of the lime-salts of fatty acids, obtained by precipitating waste soap-liquor with chloride of calcium, with addition of a small quantity of quicklime). *Dingl. pol. J.* cxlvii. 304.

1859. Hübner.—Further contributions to the manufacture of photogen, solar oil and paraffin, from lignite. *Dingl. pol. J.* cli. 119.

1859. Wagenmann.—New raw materials for the preparation of photogen and paraffin, occurring in Scotland. *Dingl. pol. J.* cli. 116.

1859. Vobl.—Examination of various bituminous materials with respect to their applicability to the preparation of illuminating materials. *Dingl. pol. J.* clii. 306, 390; cliii. 328; *Ann. Ch. Pharm.* cix. 182; *J. pr. Chem.* lxxvii. 205; *Chem. Centr.* 1859, pp. 386, 490, 517; *Rép. Chim. app.* i. 292.

1859. J. E. Hess.—Amount of photogen obtained from a peat occurring in Anhalt. *Dingl. pol. J.* cliii. 380; *Chim. Centr.* 1860, p. 164.

1859. C. Hasse.—On illuminating materials, &c., obtained by the distillation of Gallician petroleum. *Dingl. pol. J.* cli. 445; *Rép. Chim. app.* i. 292.

1859. J. Mitchel.—On the purification of paraffin. *Rep. of Patent Inventions,* April 1859, p. 300; *Dingl. pol. J.* clii. 160.—Kernot.—On the same. *London Journal of Arts,* Sept. 1859, p. 160; *Dingl. pol. J.* cliv. 64.—C. G. Müller.—On the same. *Dingl. pol. J.* cliv. 227.

1859. F. C. Calvert.—On the variations in the composition of coal-tar, according to the kind of coal from which it is obtained. *Compt. rend.* xlix. 262; *Jahresb.* 1859, p. 742.

1859. Antisell.—The manufacture of photogenic and hydrocarbon oils from coal and other bituminous substances capable of supplying burning fluids. New York and London; notice of the same by F. H. Storer. *Sill. Am. J.* [2] xxx. 112, 254.

1860. L. Unger.—On the composition and occurrence of lignites, especially adapted for the production of tar, and on the treatment of the tar for obtaining paraffin, photogen and solar oil. *Dingl. pol. J.* clv. 41; *Chem. Centr.* 1860, p. 515.—On the qualitative and quantitative differences in the tar obtained from lignite, according to its structure and mode of occurrence. *Dingl. pol. J.* clviii. 222; *Rép. Chim. app.* iii. 240.

1860. H. Perntz.—Description of the retort furnaces (for heating lignite) in the photogen and paraffin factory of Wilhelmshütte near Oscherscheben. *Dingl. pol. J.* clv. 56.

1860. C. Zincken.—On the illuminating power of the products of the distillation of lignite, &c. *Dingl. pol. J.* clv. 128, 215.

1860. Dnmoulin and Cotelle.—On a method of rendering heavy coal-tar oil adapted for illumination. *Chem. Centr.* 1860, 686.

1860. W. Schmidt.—On the quantities of illuminating oils, paraffin, &c., obtained from various kinds of Russian peat. *Chem. Centr.* 1860, p. 804.

1860. H. Schwarz.—On the applicability of Gallician petroleum to the preparation of photogen and solar oil. *Dingl. pol. J.* clvi. 464.

1861. Vohl.—On the causes of the failure of many factories of paraffin and photogen *Dingl. pol. J.* clii. 376.

1861. A. Gessner.—On coal, petroleum and distilled oils. 8vo. New York.

1862. Dnllo.—On the preparation of mineral oils and paraffin from various raw materials, *Chem. Centr.* 1862, pp. 252, 265,—being an extract from his work entitled "Die Torfverwerthung in Europa."

1862. B. H. Paul.—On the working of the bituminous peat of Lews Island (Hebrides), for the same purpose. *Chem. News*, vi. 221, 243.

1862. A. H. Chnrch.—On the oils obtained from Albertite. *Chem. News*, vi. 122; *Rép. Chim. app.* iv. 419.

1862. Perntz.—On the recovery and utilisation of the acid and alkaline liquids employed in the purification of mineral oils. *Dingl. pol. J.* clxiii. 65.

1862. Stenhouse.—Application of paraffin to the impregnation of leather and tissues, to render them air- and water-tight. *London Journal of Arts*, September 1862, p. 154; *Dingl. pol. J.* cxlvii. 72.

1863. B. H. Panl.—Destructive distillation, considered in reference to modern Industrial Arts. *Jour. Soc. Arts*, xi. 470; *Chem. News*, vii. 282, viii. 56, 78.

1863. G. Thenins.—Examination of peat from Salzhurg and lignite from Ellnbogen, with regard to their adaptability for the preparation of photogen and paraffin. *Dingl. pol. J.* clxix. 362, 467; clxx. 296, 361.

1863. H. Lahore.—Description of an apparatus with revolving retorts for the distillation of schists, asphalt, &c. *Dingl. pol. J.* clxx. 104. W. M. Williams.—Description of reverberatory furnaces for similar purposes. *Le Technologiste*, June 1863, p. 458; *Dingl. pol. J.* clxx. 106.

1863. Breitenlohner.—Process for improving heavy oils obtained from peat-tar and rendering them fit for illumination. *Dingl. pol. J.* cxlvii. 378; *Bull. Soc. Chim.* vi. 71.

1863. A W. Hofmann.—Report on chemical products and processes in the International Exhibition of 1862, pp. 138—144.

1864. B. H. Panl.—Artificial light and lighting materials. *Jour. Soc. Arts*, xii. 311; *Jour. Franklin Institute*, 1865.

See also the several volumes of *Wagner's Jahresbericht über die Fortschritte und Leistungen der chemischen Technologie*, Leipzig, 1855—1864. B. H. P.

**PARAGLOBULARETIN.** See Globularia (ii. 846).

**PARAGUAY TEA** or *Yerba-mate.*—The dried leaves and twigs of *Psoralea glandulosa*, L., *Ilex paraguayensis*, St. Hilaire. They contain caffeine, 1·1 to 1·2 per cent. according to Stenhouse (Phil. Mag. [3] xxiii. 426); 0·44 per cent. according to Stahlschmidt (Pogg. Ann. cxii. 441).

**PARAHEXYLENE.** Syn. with $\beta$ Hexylene. (See Hexylene, iii. 155.)

**PARALACTIC ACID.** Syn. with Sarcolactic Acid. (See Lactic Acid, iii. 457.)

**PARALBUMIN.** See Albumin (i. 68).

**PARALDEHYDE.** The liquid modification of aldehyde obtained by Weidenbnseh (see Aldehyde, i. 109). According to Liehen (Jahresb. 1860, p. 103), it is also produced by heating aldehyde with ethylic iodide to 100° in a sealed tube. It melts at 12°, boils at 123°—124°, and has a vapour-density of 4·71, agreeing nearly with that calculated for 2 vol. from the triple formula of aldehyde, $C^6H^{12}O^3$. It is probably identical with the modification of aldehyde which Genther and Cartmell obtained by the action of sulphurous acid upon aldehyde (melting at 10°, boiling at 124°), perhaps also with Fehling's elaldehyde. A body having the same properties, excepting that it melts at 4°, is produced by saturating aldehyde with cyanogen gas, and leaving the solution to itself in a sealed tube for some time at the ordinary temperature.

**PARALLELOSTERISM.** Compounds analogous in composition and exhibiting equal differences of atomic volume, are called by Scheerer, *parallelosteric compounds.* (See Isomorphism, iii. 432.)

**PARALOGITE.** A silicate of aluminium, calcium, and sodium, intergrown with lapis lazuli, from the neighbourhood of Lake Baikal, in white four or eight-sided prisms, harder than quartz, having a specific gravity of 2·665, and melting before the blowpipe to a colourless glass. It contains, according to Thoreld, 44·95 per cent. silica, 26·89 alumina, 14·44 lime, 10·86 soda, 1·01 potash (with 1·85 loss) (*Rammelsberg's Mineralchemie*, p. 778). According to Kokscharow, N. Petersb. Acad. Bull. i. 231), it has the same angles as mejonite, and may be regarded as a variety of scapolite.

**PARAM.** A substance isomeric with cyanamide, $CH^2N^2$, produced by the action of carbonic anhydride on sodamide. It crystallises in concentric groups of fine silky prisms, soluble in water and alcohol, melting at 100° when dry (cyanamide melts at 40°), and solidifying again in the crystalline form at about 180°. It is further distinguished from cyanamide (ii. 188) by not forming either a yellow silver compound or a brown copper compound. Cyanamide changes into param when left to itself for a long time. (Beilstein and Genther, Ann. Ch. Pharm. cviii. 88.)

**PARAMALEIC ACID.** Syn. with FUMARIC ACID (ii. 741).

**PARAMALIC ACID.** Syn. with DIGLYCOLLIC ACID. (See GLYCOLLIC ACID, ii. 912.)

**PARAMECONIC ACID.** Syn. with COMENIC ACID (i. 1103).

**PARAMENISPERMINE.** See MENISPERMINE (iii. 880).

**PARAMIC ACID.** } See MELLITIC ACID, AMIDES OF (iii. 873).
**PARAMIDE.** }

**PARAMIDOBENZOIC ACID.** Syn. with PARAOXYBENZAMIC ACID (p. 352).

**PARAMORPHINE.** Syn. with THEBAÏNE.

**PARAMORPHOUS CRYSTALS.** This term was first applied by W. Stein and afterwards adopted by Scheerer (J. pr. Chem. lvii. 60), to designate certain pseudomorphs in which a change of molecular structure has taken place without alteration of external form or chemical constitution: for example, the monoclinic crystals of fused sulphur, which gradually become opaque and are then found to be made up of crystalline particles having the trimetric form of sulphur crystallised from fusion at low temperatures (ii. 332); also crystals of arragonite (trimetric) altered internally to calcspar (rhombohedral), and of iron pyrites (monometric) altered internally to marcasite (trimetric). Scheerer also regards as paramorphs, many instances of pseudomorphism in which a change of chemical composition has taken place as well as of molecular structure, *e.g.* the crystals of scapolite occurring at Snarum and Krageroe, in Norway, which consist of crystallo-granular masses of orthoclase or albite, supposing that these minerals are dimorphous and sometimes crystallise in the form of scapolite. For a full discussion of the subject, see Scheerer's article PARAMORPHOSE in the *Handwörterbuch der Chemie*, vi. 53; also Jahresb. 1852, p. 302; 1853, p. 860; 1854, pp. 872, 888.

**PARAMUCIC ACID.** An isomeric modification of mucic acid produced by prolonged boiling of the latter with water (iii. 1057).

**PARAMYLENE** or *Diamylene.* $C^{10}H^{20}$.—A polymeric modification of amylene which passes over at 160°, when amylic alcohol is distilled with chloride of zinc.

**PARAMYLONE.** The name given by Gottlieb (Ann. Ch. Pharm. lxxv. 51) to small grains resembling wheat starch, which are contained in considerable quantity in *Euglena viridis*, a species of infusorium. They are white, insoluble in water and dilute acids, and have the composition of starch. At 200° they are converted into a tasteless gummy mass, soluble in water. Fuming hydrochloric acid converts them into glucose.

**PARANAPHTHALENE** or **ANTHRACENE.** $C^{14}H^{10}$.—A hydrocarbon discovered by Dumas and Laurent in 1832 (Ann. Ch. Phys. [2] l. 187), further examined by Laurent (*ibid.* lx. 220; lxvi. 149; lxxii. 415), Fritzsche (Ann. Ch. Pharm. cix. 249), and more completely by Anderson (Edinb. Phil. Trans. xxii. [3] 681; Chem. Soc. Qu. J. xv. 44). It is produced in the dry distillation of coal, bituminous shale and wood, and is contained in the last heavy and semifluid portions of the tar, at first together with naphthalene, finally with chrysene. A commercial product of this kind, used as a lubricator for machinery, is yellow, soft, somewhat like palm-oil, and contains, besides anthracene, a small quantity of naphthalene, and a much less volatile empyreumatic oil.

*Preparation.*—Crude commercial anthracene is distilled from an iron retort, and the colourless portions which pass over at the beginning are pressed to remove the oil, and purified by repeated crystallisation from benzene, or by sublimation. The coloured portions which pass over at a later stage of the distillation, are obtained colourless by repeated rectification, then purified in the same manner. (Anderson.)

Fritzsche immediately dissolves anthracene, obtained by pressure and recrystallisation, in boiling benzene, together with excess of picric acid, whereby crystals of the picrate are obtained on cooling. From this compound anthracene may be separated by ammonia, and purified by recrystallisation from alcohol.

*Properties.*—Anthracene forms small colourless laminæ, which exhibit a silky lustre when immersed in alcohol, but become dull when dry. The laminæ which separate from solution in benzene, are less lustrous and somewhat granular (Anderson). Anthracene melts at 213° (at 180°, according to Dumas and Laurent; at about 210°,

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according to Fritzsche) to a colourless liquid, which solidifies to a lamino-crystalline mass on cooling. It sublimes slowly at the heat of the water-bath, more quickly in thin laminæ, at a stronger heat, and distils without decomposition at a still higher temperature (Anderson), above 300° according to Dumas and Laurent. It is inodorous if free from empyreumatic oil; tasteless. Specific gravity 1·147 (Reichenbach).—Vapour-density, obs. = 6·74 at 450° (Dumas and Laurent); calc. = 6·17.

Anthracene is insoluble in *water*, but dissolves easily in boiling *alcohol*, more abundantly in *ether*, *benzene*, and *volatile oils* (Anderson), especially in *oil of turpentine* (Dumas and Laurent). It is not altered by *alkalis*. When it is dissolved together with excess of *picric acid* in boiling benzene, the liquid on cooling deposits deep ruby-coloured crystals of picrate of anthracene, $C^{14}H^{10}.C^6H^3(NO^2)^3O$. This compound melts at about 170°, and is decomposed wholly or partially by water, alcohol, and ether, which dissolve out the picric acid. (Fritzsche.)

*Decompositions.*—1. Anthracene dissolves in *oil of vitriol*, with green colour, and forms a conjugated acid.—2. In contact with *bromine*, either liquid or gaseous, it is slowly converted into hexbromanthracene.

3. Anthracene exposed to a slow current of *chlorine-gas* for not too long a time, is converted into hydrochlorate of chloranthracene, a small quantity of hydrochloric acid gas being evolved at the same time. Exposed for a short time to a rapid current of chlorine, it becomes heated, and forms hydrochloric acid and chloranthracene. When heated in chlorine gas, it absorbs a much larger quantity, gives off larger quantities of hydrochloric acid, and exhibits an increasing amount of chlorine, till after eight days, a semi-fluid product is obtained, which, by solution in ether and evaporation, is resolved into an oily and a crystallisable chlorine-compound (Anderson). The crystals are soluble in alcohol, ether and benzene; contain 47·5 per cent. C and 2·56 H, and are, perhaps, $C^{14}H^9Cl^5$ (calc. 47·39 per cent. C, 2·54 H) or perhaps a mixture. The oil treated with alcoholic potash, yields more than one crystallisable substance. (Anderson.)

4. Anthracene is but slightly attacked by cold *nitric acid*, but by boiling for several days with nitric acid of specific gravity 1·2 it is converted into oxanthracene. Nitric of specific gravity 1·4 likewise forms oxanthracene, but mixed with other products; if fuming nitric acid be added at the same time, dinitroxanthracene is also produced. These compounds separate out on cooling, whilst a crystallisable acid remains in the mother-liquor. This substance, Anderson's *anthracenic acid*, obtained by careful evaporation, is easily soluble in water, and forms crystallisable compounds with ammonia and potash, insoluble salts with baryta and oxide of lead. (Anderson.)

Laurent, by treating anthracene with nitric acid, obtained four nitro-compounds (and oxanthracene), the formulæ and independent existence of which are doubtful. (See *Gmelin's Handbook*, xvi. 166.)

### *Derivatives of Paranaphthalene or Anthracene.*

**Bromanthracenes.** (Anderson, *loc. cit.*)—When a thin layer of pulverised anthracene is placed, together with bromine, under a bell-jar, and the mass which forms after a few days is pulverised and again exposed to the bromine-vapours, this treatment being repeated as long as the bromine continues to be absorbed, and the brown mass then dissolved in benzene, the solution on cooling deposits hexbromanthracene, $C^{14}H^4Br^6$, which, when recrystallised from ether or from benzene, forms small, white, hard, apparently rhombic crystals. It is sparingly soluble in *alcohol*, *ether* and *benzene;* turns brown at 176°, and melts at 182°, with evolution of bromine. When heated with *oil of vitriol*, it melts, and gives off bromine and hydrobromic acid. It is but slightly attacked by *nitric acid*.—With *alcoholic potash* it acquires a yellow colour, and forms bromide of potassium and bromide of dibromanthracene, $C^{14}H^8Br^2.Br^2$, which, when recrystallised from *benzene*, forms long yellow needles, having a fine silky lustre, and melting, with partial decomposition, at 238°. They are nearly insoluble in cold benzene, and soluble only in benzene heated above 100°; still less soluble in *alcohol* and *ether*, either hot or cold.

**Chloranthracene.** $C^{14}H^9Cl$.—This compound, obtained by subjecting anthracene to the action of a rapid stream of chlorine for a short time only, forms small, hard, crystalline scales, soluble in alcohol, ether and benzene. (Anderson.)

*Hydrochlorate of Chloranthracene*, $C^{14}H^9Cl.HCl$.—To obtain this compound, cold chlorine gas is passed in a slow stream over anthracene, and the resulting mass is crystallised by solution in benzene and cooling. Laurent introduces pulverised anthracene into a bottle filled with chlorine, dissolves out the anthracene which remains unaltered after 48 hours, with a small quantity of boiling ether, and crystallises the undissolved portion from a large quantity of boiling ether. It forms radiate needles often very long (Anderson); yellowish, shining laminæ, fusible and volatile (Laurent). It is easily soluble in *alcohol*, to which also it gives up a small quantity of hydrochloric acid, slightly soluble in *ether*. *Alcoholic potash* converts it into chloranthracene.

**Oxanthracene.** $C^{14}H^8O^2$. *Paranaphtalèse. Anthracenuse.* (Laurent, Anderson.)—When anthracene is boiled for some days with nitric acid, a resin is formed which becomes granular on cooling, and when washed with water and recrystallised from alcohol or benzene, forms light reddish-yellow crystals of oxanthracene, fusible, volatile without decomposition, and subliming in long needles. When heated on platinum-foil, it burns with a smoky flame and without residue. It is neutral, insoluble in *water*, sparingly soluble in *alcohol*, somewhat more soluble in benzene (Anderson), nearly insoluble in boiling *ether*, and in hot *coal-tar oil* (Laurent). It dissolves in boiling *nitric acid* of specific gravity 1·4, and crystallises on cooling; also in strong *sulphuric acid*, and is reprecipitated by water (Anderson). It is not altered by hot *hydrochloric acid*, by *potash-ley* or *quick-lime*, not even when sublimed over the latter. When it is heated in a test-tube with concentrated *hydriodic acid*, white scales resembling stilbene condense in the upper part; $C^{14}H^8O^2 + 8HI = C^{14}H^{12} + I^8 + 2H^2O$? (Anderson.)

*Dinitroxanthracene*, $C^{14}H^6N^2O^6 = C^{14}H^6(NO^2)^2O^2$.—When anthracene is boiled with nitric acid, and portions of the fuming acid are added from time to time, red fumes are continuously evolved, and the anthracene is converted into a resinous mixture of oxanthracene and dinitroxanthracene. From this mixture the dinitroxanthracene may be separated, by heating with a small quantity of alcohol and cooling, as a red powder having very little of the crystalline character. (Anderson.)

**PARANICENE.** The name given by St. Evre to a solid hydrocarbon, $C^{12}H^{12}$? which he obtained by distilling chloroniceic (chlorobenzoic) acid (i. 921) with caustic lime or baryta. Fuming nitric acid converts it into a nitro-compound, $C^{16}H^{11}(NO^2)$.

**PARANICINE.** $C^{16}H^{13}N$?—A base produced by the action of sulphide of ammonium on nitroparanicene. It dissolves in acids, forming crystallisable salts, and is precipitated from the solutions in snowy flakes soluble in ether. (St. Evre. See Gerhardt's *Traité*, iii. 66.)

**PARANILINE.** $C^{12}H^{14}N^2$. (Hofmann, Proc. Roy. Soc. xii. 314.)—During the preparation of aniline on the large scale, several bases of high boiling point are produced. They are to be found in the residues which remain in the stills in which the crude aniline is rectified. By distilling these residues and fractionating the products, a variety of bases are obtained, among which may be mentioned toluylene-diamine, martylamine $C^{12}H^{11}N$, and paraniline $C^{12}H^{14}N^2$.

*Preparation.*—When the fractions boiling above 330° are treated with dilute sulphuric acid, a semisolid crystalline mass is obtained, consisting of two sulphates of different degrees of solubility, the more soluble being the sulphate of paraniline, the less soluble the sulphate of martylamine. On decomposing the more soluble salt with caustic soda, a viscid basic oil is produced, which after some days solidifies to a semi-solid crystalline mass. This is to be purified from adhering oil by pressure between folds of filtering paper, and crystallised first from water, and subsequently once or twice from boiling alcohol. Paraniline forms long white silky needles, fusible at 192°. It boils above the range of the mercurial thermometer, but distils without decomposition.

*Salts of Paraniline.*—From a solution in strong hydrochloric acid, a beautiful *hydrochlorate* crystallises in transparent six-sided plates, which when dried at 100° have the formula $C^{12}H^{14}N^2.2HCl.H^2O$. On treatment with water they are immediately converted into sparingly soluble yellow needles, which at 100° contain $C^{12}H^{14}N^2.HCl.H^2O$, and at 115°, $C^{12}H^{14}N^2HCl$.—The *platinum-salt*, $2C^{12}H^{14}N^2.H^2Cl^2.Pt^{iv}Cl^4$ (at 110°), forms yellow needles of sparing solubility.—The *nitrate*, $C^{12}H^{14}N^2.HNO^3$, forms short yellowish needles grouped in stars.—*Sulphates.* On dissolving paraniline in dilute sulphuric acid, a salt easily soluble in water is obtained, having the formula $C^{12}H^{14}N^2.H^2SO^4$. Treated with excess of base, it yields a salt containing $2(C^{12}H^{14}N^2)H^2SO^4$.

*Ethylated derivatives of Paraniline.* The action of iodide of ethyl on this base results in the formation of two ethylated bases, namely $C^{12}H^{13}(C^2H^5)N^2$ and $C^{12}H^{12}(C^2H^5)^2N^2$. C. G. W.

**PARANITROBENZOIC ACID.** Syn. with NITRODRACYLIC ACID (p. 60).

**PARANTHIN.** A name applied to certain compact varieties and white and pale blue crystals of scapolite.

**PARA-OXYBENZAMIC ACID.** $C^7H^7NO^2$. *Paramidobenzoic, Oxydracylamic* or *Amidodracylic acid.* (G. Fischer, Ann. Ch. Pharm. cxxvii. 142—Wilbrand and Beilstein, *ibid.* cxxviii. 257.)—An acid isomeric with oxybenzamic acid, produced by the action of sulphuric acid on nitrodracylate (paranitrobenzoate) of ammonium (Fischer), or by the action of tin and hydrochloric acid on nitrodracylic acid (Wilbrand and Beilstein). When 1 pt. of nitrodracylic acid (p. 60) and 2 pts. of tin are treated with concentrated hydrochloric acid, and the filtrate evaporated, colourless needles or laminæ are obtained, consisting of the compound $C^7H^7NO^2.HCl$, which by solution in ammonia and supersaturation with acetic acid, yields crystals of paraoxybenzamic acid. A quicker method is to precipitate the acid tin-solution with sodic carbonate and supersaturate the filtrate with acetic acid.* (Wilbrand and Beilstein.)

Paraoxybenzamic acid crystallises in yellowish, highly lustrous capillary crystals, which melt at 197°, and are not coloured (like oxybenzamic acid) by contact with air and water (Fischer); in reddish interlaced threads, shining crystalline tufts, or small rhombohedrons melting at 186° or 187° (Wilbrand and Beilstein). When heated with *potash*, it is resolved (more easily than oxybenzamic, less easily than phenylcarbamic acid) into carbonic anhydride and aniline. Wilbrand and Beilstein regard it, however, as identical with the latter (Chancel's carbanilic acid). When *nitrous acid* vapour is slowly passed into a boiling solution of 1 pt. paraoxybenzamic acid in 120 to 125 pts. boiling water (with other proportions a different reaction takes place) till the liquid, which becomes dark in colour and gives off nitrogen, deposits on evaporation flocks which assume a resinous consistence, the filtrate yields at a certain degree of concentration, crystals of paraoxybenzoic acid, $C^7H^6O^3.H^2O$. (Fischer.)

*Azo-paraoxybenzamic acid*, $C^{14}H^{11}N^3O^4$, isomeric with diazobenzo-oxybenzamic acid (p. 292), separates on pouring nitrous ether (alcohol saturated with nitrous acid), on a cold saturated solution of paraoxybenzamic acid, as a yellow crystalline body, which is decomposed by hydrochloric acid in the same manner as diazobenzo-oxybenzamic acid, yielding hydrochlorate of paraoxybenzamic acid and paracholorobenzoic acid (p. 344). Nitrous acid passed into a hot alcoholic solution of azo-paraoxybenzamic acid forms aldehyde, together with an acid $C^7H^6O^2$, different from salylic, and probably identical with ordinary benzoic acid (see the second equation on page 293). (Wilbrand and Beilstein.)

**PARA-OXYBENZOIC ACID.** $C^7H^6O^3$. (Saytzeff, Ann. Ch. Pharm. cxxvii. 129.)—An acid isomeric with oxybenzoic and with salicylic acid, produced by heating anisic acid with concentrated aqueous hydriodic acid to 125°—130° for twelve to sixteen hours:

$$C^8H^8O^3 \quad + \quad HI \quad = \quad C^7H^6O^3 \quad + \quad CH^3I;$$

also, according to Fischer (p. 351), by the action of nitrous acid on paraoxybenzamic acid. It crystallises from hot water (according to A. Knop's determinations) in small monoclinic prisms, exhibiting the combination ∞P . oP . ∞P∞, with the following approximate values of the angles; ∞P : ∞P in the orthodiagonal principal section, = 140°; ∞P∞ : ∞P = 110°; oP : ∞P∞ = 105° 30′; oP : ∞P = 85°. It dissolves in 126 pts. of water at 15°; more easily in hot water, alcohol, and ether; has a sour taste; contains when air-dried, 1 at. water ($C^7H^6O^3.H^2O$); becomes anhydrous at 100°; melts with partial decomposition at 210°, and solidifies between 160° and 170°. It is distinguished from salicylic acid by its melting point and solubility (salicylic acid melts at 150°, and requires 1000 pts. of cold water to dissolve it); by forming with ferric chloride a yellow precipitate soluble in excess, without violet coloration; and by the much greater facility with which it is resolved into phenylic alcohol and carbonic anhydride. From oxybenzoic acid (p. 205) it is distinguished by its crystalline form, and, according to Saytzeff, by its behaviour when heated to the subliming point (oxybenzoic acid, according to Fischer, crystallises in anhydrous rectangular prisms, melts at 200°, and sublimes almost unaltered even when quickly heated; according to Gerland, however, it splits up into carbonic anhydride and phenylic alcohol).

Paraoxybenzoic acid forms with the alkalis, easily soluble salts, difficult to crystallise; with the alkaline earths and with the oxides of zinc and cadmium, it forms salts which are likewise easily soluble, but crystallise well. The *cadmium-salt*, $C^{14}H^{10}Cd''O^6.4H^2O$, crystallises in large well-defined rhombohedrons; the *silver-salt*, $2C^7H^5AgO^3.5H^2O$, crystallises from boiling water in long needles.

**PARAPECTIC ACID** and **PARAPECTIN.** See PECTIC ACID and PECTIN.

**PARAPHOSPHORIC ACID.** A name of dibasic phosphoric acid (see PHOSPHORUS, OXYGEN-ACIDS OF).

**PARAPICOLINE.** $C^{12}H^{14}N^2$? (Anderson, Ann. Ch. Pharm. lx. 86.)—A

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* Nitrobenzoic acid treated in like manner with tin and hydrochloric acid, yields the double salt $C^7H^7NO^2.HCl.Sn''Cl^2$, which, by successive treatment with sulphydric acid, ammonia and acetic acid, may be converted into oxybenzamic acid. The conversion of nitrobenzoic acid into oxybenzamic acid, may also be effected by hydrochloric acid and zinc. Nitrodracylic (paranitrobenzoic) acid is not acted upon by zinc and hydrochloric acid. (Wilbrand and Beilstein.)

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base poylmeric with picoline ($C^6H^7N$), obtained by treating picoline with $\frac{1}{4}$ to $\frac{1}{5}$ of its weight of sodium at the boiling heat for several days, treating the brown resinous mass thereby produced with water, which dissolves soda and leaves a heavy viscid oil, washing the latter with water, distilling, collecting apart the oil which passes over it at a high temperature, and rectifying.

The action of the sodium in the conversion of picoline into parapicoline has not been exactly made out. A large portion of the metal remains unaltered; part of it however enters into combination, probably forming the compound $C^6H^6NaN$ (no evolution of hydrogen was however observed), which is subsequently converted into parapicoline, as shown by the equation:

$$2C^6H^6NaN \quad + \quad 2H^2O \quad = \quad C^{12}H^{14}N^2 \quad + \quad 2NaHO.$$

Parapicoline, obtained as above, is an oil of specific gravity 1·077, and boiling between 260° and 315°. It is insoluble in water, soluble in all proportions in alcohol, ether, and oils, and has a peculiar odour different from that of picoline, but resembling that of the bases obtained from bone-oil at very high temperatures. It blues reddened litmus, is partially resinised by strong nitric acid, and forms with cupric sulphate an emerald-green precipitate, the green solution of which in hydrochloric acid contains a double salt.

The salts of parapicoline are for the most part uncrystallisable. The *hydrochlorate* is a resin easily soluble in water.—The *chloro-aurate* is yellow, amorphous, not decomposed at the boiling heat.—The *platinum-salt* has the formula $C^{12}H^{14}N^2.H^2Cl^2.Pt^{iv}Cl^4$.—*Mercuric chloride* forms with the alcoholic solution of parapicoline an abundant curdy precipitate, insoluble in water and in alcohol, easily soluble in hydrochloric acid.—The *nitrate* remains on evaporation as a syrupy liquid, which slowly solidifies to a mass of needle-shaped crystals.—The *sulphate* is a gummy mass, easily soluble in water, less soluble in alcohol.

**PARARHODEORETIN.** See Jalapin (iii. 438).

**PARASACCHAROSE.** A modification of cane-sugar, $C^{12}H^{22}O^{11}$, said to be produced under certain circumstances when a solution of sugar-candy and phosphate of ammonium is exposed to the air in the summer season, between June and September. It is crystallisable, and has a greater dextro-rotatory power than cane-sugar. (V. Jodin, Compt. rend. liii. 1252; lv. 720; lvii. 434; Rép. Chim. app. iv. 38; Bull. Soc. Chim. 1863, p. 93; 1864, p. 278; Jahresb. 1861, p. 722; 1862, p. 472; 1863, p. 572.)

**PARASALICYL.** *Salicylide of Benzoyl*, $C^{14}H^{10}O^3 = C^7H^5O^2.C^7H^5O$; also called *Spirin*. (See Salicylides.)

**PARASITES.** Chatin (Compt. rend. lvii. 771) adduces several examples which seem to show that parasitical plants possess the power of altering the juice of the plants on which they grow. Thus misletoe (*Viscum album*) growing on the oak does not contain a trace of quercitannic acid; *Loranthus* growing on *Strychnos* is not poisonous; *Hydnora*, a parasite growing on African *Euphorbiaceæ*, is used as food; *Orobanche* does not exhibit the narcotic properties of hemp; and the red juice of *Cytinus* is not found in the *Cistus* on which it grows. Chatin finds moreover that *Cytineæ* and orobanchs give off carbonic acid in sunshine, and hence concludes that phanerogamous parasites which are not green-coloured, alter the juice of the mother-plant. On the other hand, green perfect parasites (*Viscum*), and more or less coloured semi-parasites (*Melampyrum arvense*) decompose carbonic acid like other plants.

**PARASORBIC ACID.** See Sorbic Acid.

**PARASTILBITE.** A zeolite from Thyrill on the Hvalfjordr in Iceland, containing, according to v. Waltershausen, 61·87 per cent. silica, 17·83 alumina, 7·32 lime, 2·00 soda, 1·78 potash, and 9·20 water (= 200), which may be represented approximately by the formula $M^2O.2SiO^2 + \overset{\prime\prime\prime}{Al}{}^2O^3.4SiO^2 + 3H^2O$.

**PARASULPHATAMMON.** See Sulphamide.

**PARATARTARIC ACID.** Syn. with Racemic Acid.

**PARATARTRAMIDE.** Syn. with Racemamide.

**PARATARTRALIC ACID.**
**PARATARTRELIC ACID.** } Syn. with Racemic Acid.

**PARATARTROVINIC ACID.** Syn. with Ethyl-racemic Acid (see Racemic Ethers).

**PARATHIONIC ACID.** An acid isomeric with ethyl-sulphuric acid, not known in the free state, but produced as a barium-salt, when a solution of barytic ethyl-sulphate is boiled. The liquid then becomes turbid and acid, depositing sulphate of barium, and if the deposit be removed and the filtrate saturated with carbonate of barium, a crystallisable barium-salt is obtained having the composition of ethylsulphate of barium, $C^4H^{10}Ba''S^2O^8$, but distinguished from that salt by not decomposing when its aqueous solution is boiled. When calcined, it swells up like the isethionate (iii. 131), but at the same time gives off vapours of heavy wine-oil, takes fire, and then burns quietly. (Gerhardt, Compt. Chim. 1845, p. 176.)

**PARATOLUENE** or **PARATOLUOL.** A hydrocarbon, isomeric or polymeric with toluene (hydride of benzyl, i. 573), supposed by Church (Chem. News, Dec. 31, 1859; Zeitschr, Ch. Pharm. 1860, p. 144) to exist in light coal-tar oil. It boils at 119·5°; toluene at 103·7°.

**PARELLIC ACID** or **PARELLIN.** $C^9H^6O^4$? (Schunck, Ann. Ch. Pharm. liv. 274.)—An acid sometimes obtained, together with lecanoric acid, in the preparation of the latter. The lichens may be exhausted with boiling water; the solution evaporated to dryness after boiling for some time; the residue digested in boiling water, which dissolves the orsellinic ether (p. 236) produced by the mutual action of the alcohol and the lecanoric acid; and the undissolved portion taken up by boiling alcohol. The alcoholic solution on cooling deposits parellic acid in the crystalline form.

Parellic acid forms colourless needles, very slightly soluble in cold *water*, soluble in *alcohol* and in *ether*; the crystals deposited by slow evaporation are usually brilliant and very heavy. The alcoholic solution has a very bitter taste, and reddens litmus: water precipitates the parellic acid from it in the form of a jelly. The crystals give off 6·51 per cent. water at 100°, and the dried acid yields by analysis 60·7—61·8 per cent. carbon and 3·4 hydrogen, the formula $C^9H^6O^4$ requiring 60·7 carbon and 3·3 hydrogen. The acid is perhaps produced by the metamorphosis of lecanoric acid; thus:—

$$\underset{\text{Lecanoric acid.}}{C^{16}H^{14}O^7} = \underset{\text{Parellic acid.}}{C^9H^6O^4} + \underset{\text{Orcin.}}{C^7H^8O^2} + H^2O.$$

Schunck represented parellic acid by the formula $C^{24}H^7O^9$.

Parellic acid melts when heated, and at a higher temperature gives off an oil which solidifies on cooling; also a sublimate of long needles. By prolonged boiling with *water* it yields a yellow, bitter, uncrystallisable substance. It is not altered by boiling *alcohol*. It is decomposed by hot *nitric acid*, with evolution of nitrous vapours and formation of oxalic acid. *Acetic acid* dissolves it more easily than water. When heated with caustic *potash* it swells up, and is converted into a gelatinous mass which gradually dissolves, and the solution yields with mineral acids a gelatinous precipitate of parellic acid. But if the alkaline solution be previously boiled, it does not yield any precipitate on addition of an acid, but after some time deposits small, shining, octahedral crystals, which melt in boiling water before dissolving, are easily soluble in cold alcohol, and separate again on evaporation; they dissolve also in caustic baryta, forming a solution which deposits carbonate of barium when boiled. *Baryta* and *lime* act on parellic acid like potash. *Ammonia* dissolves less of it than potash; the solution when evaporated gives off ammonia and leaves crystalline parellic acid; prolonged boiling, however, is attended with decomposition.

Parellic acid decomposes *carbonates*. Its alcoholic solution precipitates *cupric acetate* and *neutral acetate of lead*. It does not precipitate *nitrate of silver*, but on addition of ammonia, a yellowish precipitate is formed which is reduced to the metallic state by boiling. An aqueous solution of parellic acid mixed with *chloride of gold* is not altered by boiling; but this salt is slowly reduced by a solution of parellic acid in potash.

*Parellate of barium* obtained by treating the acid with baryta-water, or by double decomposition, is a white powder insoluble in water. The *copper-salt* is a yellowish-green precipitate. The *lead-salt*, $C^{18}H^{10}Pb''O^8$ (?), is precipitated in large quantity in white flocks on mixing the alcoholic solution of parellic acid and neutral lead acetate. The alcoholic solution of parellic acid also forms a copious precipitate with basic acetate of lead.

**PARGASITE.** Crystallised and granular hornblende of high lustre and rather dark green colour, containing alumina, iron, and magnesia; found at Pargas in Finland and at Phipsburg and Parsonsfield in the State of Maine. (See HORNBLENDE, iii. 170.)

**PARICINE.** An alkaloïd said by Winckler (Buchn. Repert. [2] xlii. 29) to be contained in *China Jaen. fusca*, a cinchona-bark imported from Para.

**PARIDIN.** $C^8H^{10}O^3$? (Walz, Pharm. Centr. 1841, p. 690; further N. Jahresb. Pharm. xiii. 174.—Delffs, *ibid.* lx. 25.)—A neutral substance extracted from the leaves of *Paris quadrifolia*, by exhausting them with water containing acetic acid, treating the residue with alcohol, and the alcoholic extract with ether to remove chlorophyll and fatty matters, digesting the residue, together with animal charcoal, in alcohol of 0·920, filtering, removing the alcohol by distillation, drying the residue, and redissolving it in boiling water. Paridin is then deposited after a while in thin shining laminæ, forming when dry a coherent satiny mass (Walz); from cold dilute alcohol it crystallises in tufts of needles (Delffs). 100 pts. of water dissolve 1½ pt. paridin; 100 pts. alcohol of 94·5 per cent. dissolve 2 pts.; and 100 pts. of ordinary spirit dissolve 6 pts. It gives off 6·8 per cent. water at 100°. The dried substance contains, according to L. Gmelin, 55·51 per cent carbon and 7·76 per cent. hydrogen, agreeing nearly with the formula $C^6H^{10}O^3$, which requires 55·39 per cent. carbon and 7·69 hydrogen. Delffs gives the formula $C^{16}H^{28}O^7$; Walz in his last communication assigns to paridin the formula $C^{32}H^{56}O^{14}$.

Paridin is immediately coloured red by strong sulphuric or phosphoric acid; decomposed by hot nitric acid; dissolved, without coloration, by hydrochloric acid; decomposed by potash.

**PARIDOL.** $C^{26}H^{46}O^9$.—A substance formed together with glucose by boiling a solution of paridin in hydrochloric acid with dilute alcohol (Walz):

$$C^{32}H^{56}O^{14} + H^2O = C^{26}H^{46}O^9 + C^6H^{12}O^6.$$

**PARIETIC ACID.** The name given by Thomson to the acid contained in *Parmelia parietina*, afterwards shown to be chrysophanic acid (i. 958).

**PARIETIN.** Thomson's name for the yellow colouring matter of *Parmelia parietina*, which is identical with usnic acid (*q. v.*).

**PARIGLIN.**
**PARILLIC ACID.** } Syn. with SALSIPARIN or SMILACIN (*q. v.*).

**PARIS BLUE.** This name is sometimes used to designate pure Prussian blue (ferric ferrocyanide), (ii. 227), but has lately been applied to a very pure bright blue colour obtained by heating aniline with stannic chloride.

**PARIS LAKE.** Syn. with CARMINE-LAKE (i. 804).

**PARIS RED.** A name sometimes applied to very finely divided and carefully prepared ferric oxide, used for polishing optical glasses, daguerreotype plates, gold and silver ornaments, &c.

**PARISITE.** *Mussonite.*—A mineral from the emerald mines of the Musso Valley, New Granada, consisting of the carbonates of cerium, lanthanum and didymium, with fluoride of cerium and calcium. It is found crystallised in elongated double six-sided pyramids with truncated apex; basal angle 164° 58′; pyramidal angle 120° 34′. Cleavage basal, very perfect. Hardness = 4·5; specific gravity = 4·35. It has a vitreous lustre, pearly or resinous on the cleavage-faces, and a brownish-yellow colour: streak yellowish-white.

*Analyses: a, b,* by Bunsen (Ann. Ch. Pharm. liii. 147).—*c* by H. Deville and Damour (Bull. Soc. Chim. 1864, ii. 339).

| | $CO^2$ | CeO | DiO | LaO | CaO | MnO | $CaF^2$ | $CeF^2$ | $H^2O$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *a.* | 23·51 | 59·44 | | | 3·17 | . . | 11·51 | . . | 2·38 | = | 100·01 |
| *b.* | 23·64 | 60·26 | | | 3·15 | . . | 10·53 | . . | 2·42 | = | 100 |
| *c.* | 23·48 | 42·52 | 9·58 | 8·26 | 2·85 | trace | 10·10 | 2·16 | trace | = | 98·95 |

The last analysis may be pretty nearly represented by the formula $\left.\begin{matrix}2Ce\\ Di\\ La\end{matrix}\right\}C^3O^9.(Ca;Ce)F^2$, which requires 24·61 $CO^2$, 40·27 CeO, 10·44 DiO, 10·44 LaO, and 14·54 $CaF^2$.

**PARISTYPHNIN.** $C^{38}H^{64}O^{18}$? (Walz. N. Jahrb. Pharm. xiii. 355.)—A bitter substance contained, together with paridin, in *Paris quadrifolia*, and prepared from the mother-liquor of that substance by precipitating with tannic acid, separating the tannic acid from the resulting resinous precipitate by means of lead-oxide, and purifying the bitter substance from still adhering paridin by repeated solution in water, and concentration, the paridin then crystallising out. Paristyphnin is thus obtained as an amorphous mass, which is resolved by boiling with water into glucose and paridin:

$$C^{38}H^{64}O^{18} + 2H^2O = C^{32}H^{56}O^{14} + C^6H^{12}O^6.$$

**PARMELIA.** See Lichens (iii. 587).—*Parmelia ceratophylla* var. *physodes* also called *Parmelia physodes*, contains two neutral substances, *physodin* and *ceratophyllin* (see PHYSODIN).

**PARMEL-RED** and **PARMEL-YELLOW** are colouring matters contained in *Parmelia parietina.* The latter is chiefly chrysophanic acid, and the former appears to be produced from it.

**PARTHENIC ACID.** The name given by Peretti to the acid which forms in distilled chamomile water after long keeping. It is said to form a crystalline calcium-salt.

**PARTING.** The separation of gold from silver by means of nitric acid (ii. 929, 932).

**PASSIVE STATE OF METALS.** See Electricity (ii. 430).

**PASTE** or **STRASS.** A kind of glass used in the manufacture of artificial gems. See Glass (ii. 841); also *Ure's Dictionary of Arts,* &c. (iii. 407).

**PASTINACINE.** A peculiar substance, probably an alkaloïd, said by Wittstein (Buchn. Repert. xviii. 15) to exist in the seeds of the parsnep (*Pastinaca sativa*).

**PASTO-RESIN.** $\mathrm{C^{10}H^8O^2}$.—A resinous substance of unknown origin, imported from South America, where, according to Boussingault, it is used by the Pasto Indians for varnishing wood. It is viscid and capable of being extended into very tenacious films, which gradually harden without becoming brittle. It is destitute of taste and smell, has a vitreous fracture, and is heavier than water. When heated above 100°, it becomes elastic like caoutchouc, takes fire and burns with a smoky flame. Alcohol and ether extract from it a small quantity of green resin, and leave a strongly tumefied mass, perfectly soluble in caustic potash. Oil of turpentine does not act upon it; strong sulphuric acid dissolves it without decomposition. (Boussingault, Ann. Ch. Pharm. lvi. 217.)

**PATCHOULI.** *Pachupat* or *Patscha-pat.*—The herb of *Pogostemon Patchouli,* L., a labiate plant indigenous in the East India Islands, and employed, on account of its pungent odour, like that of *Chenopodium anthelminticum,* for preserving fur from the attacks of insects; also in perfumery. When distilled it gives off about 2 per cent. of volatile oil. It also contains tannin and a green odorous resin.

The volatile oil of patchouli is brownish-yellow, somewhat viscid like olive-oil, has a specific gravity of 0·9554 at 15·5°, and yields at 257° a hydrocarbon resembling oil of cubebs; the portion which boils at a higher temperature contains the blue substance called cœrulein (see Oils, Volatile, p. 185). For the refractive power of patchouli-oil, see the table, p. 186.

**PATINA.** *Antike patina, Patina antique,* or *Patina verte.*—These names are applied to the hard green or blue-green deposit of cupric carbonate, having the composition of malachite ($\overset{''}{\mathrm{Cu}}{}^2\mathrm{CO^4.H^2O}$) which forms on copper or bronze that has been exposed to moist air for a long time, or has lain for years underground. It is imitated artificially by wetting the surface of the metal with dilute solutions of acetic acid, nitrate of copper, sal-ammoniac, salt of sorrel, &c., and exposing it to the air. That the deposit may have the requisite hardness, it must be formed slowly, and hence it is necessary to use dilute solutions. (See *Handworterbuch d. Chemie,* vi. 100.)

**PATRINITE.** Syn. with Aciculite.

**PAULITE.** A variety of hypersthene from the island of St. Paul, on the coast of Labrador. Specific gravity 3·389. Contains 51·36 per cent. silica, 0·37 alumina, 21·31 magnesia, 21·27 ferrous oxide, 1·32 manganous oxide, and 3·09 lime (= 98·72). (Damour, Ann. Min. [4] v. 147.)

**PAULOWNIA IMPERIALIS.** A colouring matter has been obtained from the capsules of this plant by Belhomme (Compt. rend. xlvii. 214); but no particulars have been published respecting it.

**PAVIETIN.** *Fraxetin* (ii. 707).—According to recent experiments by Rochleder (J. pr. Chem. xc. 433), this substance, produced by the decomposition of paviin from horsechestnut bark (*vid. inf.*), has the composition $\mathrm{C^{10}H^8O^5}$. It has a lemon-yellow colour, becomes straw-yellow at 120°, and is converted by sublimation at 200° into a mass of woolly crystals. It has an acid reaction and combines with bases.

**PAVIIN.** *Fraxin* (ii. 708).—This substance is contained in that portion of the precipitate formed by neutral acetate of lead in the aqueous decoction of horsechestnut bark, which is soluble in water containing acetic acid. Its composition, as determined by analysis, is $\mathrm{C^{64}H^{74}O^{41} = 4C^{16}H^{18}O^{10}.H^2O}$. When heated in a stream of carbonic anhydride to 150° it becomes anhydrous (more quickly at 200°), and has then the composition $\mathrm{C^{16}H^{18}O^{10}}$. Paviin at 117° is pale-yellow, amorphous, easily friable and still contains water; it melts at 190°. When recrystallised from hot alcohol it is pure white and gives off its water between 110° and 113°. By boiling with dilute acids, it is resolved into glucose and pavietin or fraxetin, according to the equation:

$$\mathrm{C^{16}H^{18}O^{10} \quad + \quad H^2O \quad = \quad C^{10}H^8O^5 \quad + \quad C^6H^{12}O^6},$$

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according to which, 100 pts. paviin should yield 55·5 pts. pavietin; the quantity found was 55·2. (**Rochleder**, *loc. cit.*)

**PEA.** *Pisum sativum.*—The composition of the seed and straw of this plant has been investigated by several chemists.

The following determinations of the nitrogen, fat, ash, and water in fresh pea-seeds are by **Ward** and **Eggar**, made under **Way**'s direction (Agr. Soc. J. vol. x. pt. 2; Jahresb. 1849, p. 708):

| | Nitrogen per cent. | Fat per cent. | Water per cent. |
|---|---|---|---|
| White or garden peas, grown on clay soil . . . . | 3·57 | 1·01 | 15·40 |
| White or garden peas, grown on sandy soil . . . . | 2·97 | . . | 13·60 |
| Grey or field peas, grown on clay soil . . . . | 3·47 | 1·54 | 16·60 |
| Grey or field peas, grown on sandy soil . . . . | 3·28 | 1·04 | 16·40 |

**Poggiale** (J. Pharm. [3] xxx. 180, 255; Jahresb. 1856, p. 808) found in common green peas, dried and shelled, 57·7 per cent. starch, dextrin and sugar, 21·7 nitrogenous substance (legumin), 1·9 fatty matter, ·2·8 ash-constituents, 3·2 cellulose, and 12·7 water.

**W. Mayer** (Ann. Ch. Pharm. ci. 129; Jahresb. 1857, p. 637) has made the following determinations of the water, phosphoric anhydride, nitrogen and ash in garden and field peas:

| | Air-dried. | Dried substance. | | |
|---|---|---|---|---|
| | $H^2O$. | $P^2O^5$. | N. | Ash. |
| Selected peas from the garden of the Agricultural Society at Munich . . . . . . | 9·58 | 1·458 | 4·87 | 3·45 |
| Bohemian field peas . . . . . . | 8·99 | 1·408 | 4·81 | |
| Field peas from Schleissheim, Upper Bavaria (calcareous soil) . . . . . . | 13·62 | 1·025 | 4·25 | 2·91 |

The shells of peas weigh from 0·8 to 1 per cent. as much as the seed. The weight of straw is about 2·7 times as much as that of the seed, or 27 pts. seed to 73 pts. straw in 100 pts. of total weight (**Schwerz**). 100 pts. of pea-straw contain 12 pts. nitrogenous matter, 21·9 matter soluble in potash, 47·5 per cent. non-azotised matter insoluble therein, 6·0 ash, and 12·0 water.

**Way** and **Ogston** (Agr. Soc. J. vol. vii. pt. 2; Jahresb. 1849, p. 672) found in peas of various kinds (air-dried) from 13·6 to 17·5 per cent. water; and the peas dried at 100° were found to contain 0·25 to 0·372 per cent. sulphur, and 2·39 to 2·68 per cent. ash.

In the straw of garden-peas (air-dried) the same chemists found 15·38 to 15·64 per cent. water; that of white peas dried at 100°, yielded 8·92 to 9·40 per cent. ash; that of grey peas 6·5 to 7·5 per cent.

The composition of the ash of peas and pea-straw, as determined by Way and Ogston, is given in the table, p. 359.

The ash of pea-straw has also been analysed by **Hertwig**, with the following results:

*a.* Pea-straw from Duderstadt; *b.* from Thuringen.

| | *a.* | *b.* | | *a.* | *b.* |
|---|---|---|---|---|---|
| Carbonate of Potassium . | 4·1 | 4·3 | Magnesia . . . | 4·0 | 1·4 |
| Carbonate of Sodium . | 8·3 | | Phosphate of Calcium . | 5·1 | 1·1 |
| Sulphate of Potassium . | 10·7 | 12·0 | Phosphate of Magnesium . | 4·4 | 7·8 |
| Chloride of Sodium . | 4·6 | 3·7 | Ferric and Aluminic Phosphates . . | 2·1 | 3·6 |
| Silica . . . . | 7·8 | 15·5 | | | |
| Carbonate of Calcium . | 47·8 | 49·7 | | 98·9 | 99·1 |

For numerous other analyses of the ash of peas and pea-straw, made chiefly at the instigation of the Prussian Agricultural College, see **Liebig** and **Kopp**'s Jahresbericht, i. 1074, Table A. Nos. 5, 6, 7, 8, 10, 11; and ii. 656, Table B. Nos. 1—32.

**PEACH.** See FRUIT (ii. 715).

**PEACOCK COPPER ORE.** Syn. with PURPLE COPPER. (See COPPER, SULPHIDES OF, ii. 78.)

**PEARL.** A highly prized spherical concretion found within the shell of the pearl-oyster. These molluscs are subject to a kind of disease, caused by the introduction of foreign bodies within their shells. In this case the inner layer of the shell, the mother-of-pearl (p. 322), instead of being spread in thin layers on the inside of the shell, accumulates round these particles in concentric layers, forming pearls. These concretions consist of carbonate of calcium interstratified with cellular membrane. They have a bluish-white colour, with considerable lustre and iridescence. The most valuable pearl fisheries are on the coast of Ceylon, and at Olmutz in the Persian Gulf.

Composition of the Ash of Grain and Straw of Peas.

| | Way. | | | | Ogston. | | | Way and Ogston. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | White peas. | | | | Early white peas. | | | Grey peas or prolific maple (grain). | | | Straw from | | | |
| | On chalk soil. | | On clay soil. | | Seed-peas. | Grown from the last. | | Seed-peas. | Grown from the last. | | White peas. | | Grey peas. | |
| | Grain. | Straw. | Grain. | Straw. | | On clay soil. | On sandy soil. | | On clay soil. | On sandy soil. | On clay soil. | On sandy soil. | On clay soil. | On sandy soil. |
| Potash | 44·02 | 3·87 | 41·50 | 12·68 | 35·43 | 40·40 | 39·22 | 42·43 | 41·70 | 42·00 | 13·22 | 17·50 | 21·30 | 16·63 |
| Soda | 6·97 | 1·86 | 5·02 | 0·24 | 0·44 | 0·21 | . . | 3·27 | . . | . . | 0·95 | 0·86 | 4·22 | 3·90 |
| Lime | 6·97 | 46·92 | 4·55 | 36·46 | 6·16 | 7·03 | 6·41 | 5·73 | 4·78 | 7·81 | 38·61 | 39·72 | 37·17 | 36·47 |
| Magnesia | 6·66 | 8·36 | 6·96 | 5·73 | 7·03 | 7·33 | 6·61 | 5·92 | 5·78 | 6·77 | 8·27 | 4·25 | 7·17 | 7·22 |
| Ferric oxide | 0·25 | 1·14 | trace | 0·73 | 0·64 | 0·76 | 1·21 | 0·44 | 0·18 | 0·30 | 1·57 | 2·63 | 1·07 | 1·80 |
| Sulphuric acid ($SO^3$) | 4·70 | 1·85 | 5·85 | 2·26 | 6·70 | 4·04 | 7·26 | 6·23 | 4·47 | 5·38 | 8·62 | 4·13 | 8·69 | 1·22 |
| Silica | 1·76 | 2·53 | 0·84 | 1·94 | 1·76 | 1·12 | 1·55 | 1·74 | 0·68 | 0·62 | 6·67 | 5·48 | 3·23 | 6·10 |
| Carbonic acid ($CO^2$) | 3·18 | 30·33 | 2·12 | 29·03 | 0·98 | 1·16 | 1·95 | 4·38 | 0·82 | 1·60 | 9·46 | 18·72 | 12·48 | 18·28 |
| Phosphoric acid ($P^2O^5$) | 24·20 | 1·31 | 28·85 | 1·23 | 38·05 | 37·93 | 35·66 | 29·92 | 36·50 | 30·82 | 5·38 | 3·78 | 4·65 | 4·18 |
| Chloride of Potassium | . . | . . | . . | . . | . . | . . | . . | . . | 3·82 | 4·70 | | | | |
| Chloride of Sodium | 8·23 | 1·76 | 4·30 | 9·66 | 2·81 | . . | . . | . . | 1·24 | . . | 7·22 | 2·90 | . . | 4·16 |
| Sum | 106·94 | 99·93 | 99·99 | 99·96 | 100·00 | 99·98 | 99·87 | 100·06 | 99·97 | 100·00 | 99·97 | 99·97 | 99·98 | 99·96 |
| Ash per cent. in dry substance | 2·93 | 8·92 | 2·68 | 9·40 | 2·40 | 2·38 | 2·48 | 2·60 | 2·87 | 2·56 | 7·61 | 7·50 | 6·53 | 7·50 |
| Ash per cent. in fresh substance | 1·97 | 7·52 | 2·25 | 7·96 | 2·84 | 2·77 | 2·87 | 2·24 | 2·40 | 2·14 | 6·71 | 7·03 | 5·79 | 6·86 |

**PEARL-ASH.** Partially purified carbonate of potassium, prepared from the ashes of plants (see CARBONATES, i. 790).

**PEARL-MICA.** Syn. with MARGARITE.

**PEARL-SINTER** *or Fevrite.*—A variety of opal occurring in the cavities of volcanic tufa (see OPAL, p. 204).

**PEARL-SPAR.** This name is applied to rhombohedral crystallisations of dolomite (magnesio-calcic carbonate) having curved faces and a pearly lustre; when the crystals are not curved, and have a brown or reddish-brown colour, they are called *brown spar:* the latter variety contains from 5 to 10 per cent. oxide of iron or manganese.

**PEARL-STONE.** A felspathic mineral, having a pearly lustre, occurring in spherules or spheroïdal concretions. Specific gravity 2·3 to 2·4. A specimen from Hungary analysed by Erdmann gave 72·87 per cent. silica, 12·05 alumina, 1·75 ferric oxide, 1·30 lime, 1·10 magnesia, 6·13 potash and soda, and 3·00 water (= 98·20).

**PEASTONE** or **PISOLITE.** A calcareous rock consisting of spherical grains like oolite, but differing therefrom by the larger size of its particles, which are composed of concentric laminæ.

**PEAT.** *Torf; Tourbe.*—This product of the natural alteration of plant-tissues is of frequent occurrence in places where the presence of stagnant water or a very humid atmosphere and certain other conditions have favoured the growth of mosses and marsh plants, together with certain kinds of grass, heath, &c. The remains of these plants, gradually accumulated and chemically altered to a greater or less extent, often constitute beds of considerable extent, varying in thickness from a few inches to many feet.

There are many kinds of peat, presenting very great diversity in their texture, colour, and most other characters; some varieties consist almost entirely of withered remains of plants which have undergone but little alteration except mechanically; in other varieties the organised structure of the plant remains more or less distinctly recognisable, and in other kinds there is no obvious indication of plant-structure remaining. Peat of the former kind is generally of a pale yellowish-brown colour, very bulky and retentive of water; when dried it is very light and spongy, somewhat resembling compressed hay, and its specific gravity is often as low as 0·25. Peat of the latter kind, on the contrary, is either black or dark brown, and in its natural state has a clayey consistency without any fibre, so that it can sometimes be wrought into tiles or pipes for draining purposes; when such peat is dried, it shrinks considerably, and becomes denser than water, very good kinds having sometimes a specific gravity of 1·25. Between these two extremes numerous intermediate kinds of peat are met with. In the natural state, peat is always mechanically mixed with a very large proportion of water, varying from eighty to upwards of ninety per cent. by weight, the fibrous kinds always containing the largest amount of water. When the water is separated by drying the peat in thin slices in the air, a quantity still remains which is not separable by air-drying, and amounting generally to 15 or 30 per cent. of the air-dried material.

The large amount of water mixed with peat in its natural state is the most serious obstacle to the useful application of this material upon any extensive scale, as fuel and for other purposes, for the practical difficulties of separating this water by air-drying rapidly increase in proportion to the extent upon which the peat is collected. The hygroscopic water still remaining in air-dried peat is also highly prejudicial to its utility as fuel. Hence it is that wherever coal can be obtained at a moderate cost, not exceeding ten shillings per ton, it is impossible to use peat as fuel with advantage, and it may be preferable to use coal even where it costs as much as twenty shillings per ton, when the peat is far distant from the place where fuel is required, inasmuch as the carriage of peat, which has a much smaller fuel-value than coal, will often make its cost equal to that of an equivalent quantity of coal. (See FUEL, ii. 723.)

The composition of dry peat presents differences as great as those existing between the several kinds in other respects.

The amount of ash in peat is very variable, as will be seen from the following table, and there are equally great differences in the composition of these ashes. It is very rarely that the composition of peat-ash is such as to admit of the opinion that it represents merely the mineral constituents of the plants from whose remains the peat has been formed. In most cases a large portion of this ash is referrible either to mere mechanical admixture of earth, or to the deposition of mineral substances from water permeating the peat, and consequently the composition of the ash is much influenced by the nature of the prevailing rocks in the neighbourhood of peat-deposits, or such parts of those rocks as are carried away either mechanically or chemically by the action of water. The permeation of peat by water probably exercises a further influence in altering the composition of its mineral or ash constituents, by abstracting certain substances, in virtue either of a kind of dialysis or of chemical reaction. Such being the case, the composition of peat-ashes and the nature of the changes they have undergone would be determined mainly by local conditions, and in this way the great diversity of composition which is found to exist may be to some extent accounted for.

When air-dried peat is exposed to a temperature of 100° C., it generally loses from 15 to 30 per cent. of its weight, consisting chiefly of hygroscopic water; but, according to Marsilly, some decomposition takes place even at that temperature, and volatile products containing carbon and hydrogen are evolved in small quantity. At higher temperatures peat is entirely decomposed, yielding the ordinary products of dry or destructive distillation, viz. gas, tar, a watery liquid, and a carbonaceous residue. These products and their constituents are, in their general character, intermediate between the analogous products obtained under similar conditions from wood and from bituminous minerals, their relative amount, chemical nature, &c., being dependent upon the temperature at which the decomposition takes place, as in all other cases of destructive distillation. The several products of the distillation of peat also vary to some extent both in quantity and quality according as the peat approximates more, on the one hand, to unaltered wood, or on the other hand to coal, just in the same manner as there are similar differences of degree between the products of different bituminous minerals.

COMPOSITION OF PEAT.

| | Specific gravity. | Water in air-dried peat. | Percentage composition of peat dried at 100° C. | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Ash. | Authority. |
| Cappoge | . . | . . | 51·05 | 6·85 | 39·55 | | 2·55 | Kane |
| Kilbeggan | . . | . . | 61·04 | 6·67 | 30·46 | | 1·83 | |
| Kilbaba | . . | . . | 51·13 | 6·33 | 34·48 | | 8·06 | |
| Phillipstown | 0·405 | . . | 58·69 | 6·97 | 32·88 | 1·45 | 1·99 | Sullivan and Gages |
| | 0·669 | . . | 60·48 | 6·10 | 32·55 | 0·88 | 3·30 | |
| Wood of Allen | 0·335 | . . | 59·92 | 6·61 | 32·22 | 1·26 | 2·74 | ,, |
| | 0·639 to 0·672 | . . | 61·02 | 5·77 | 32·40 | 0·81 | 7·90 | ,, |
| Devon | 0·850 | 25·56 | 54·02 | 5·21 | 28·17 | 2·30 | 9·73 | Vaux |
| Island of Le | 1·130 | 23·20 | 60·00 | 6·90 | 30·00 | 1·30 | 1·90 | Paul |
| Brésles | 0 | 2·17 | 46·80 | 5·65 | 41·15 | | 6·40 | Marsilly |
| | . . | 3·14 | 47·48 | 7·16 | 36·06 | | 9·00 | ,, |
| Thésy | . . | 3·07 | 50·67 | 5·76 | 36·95 | 1·92 | 6·70 | ,, |
| | . . | 7·20 | 43·65 | 5·79 | 36·66 | | 14·00 | ,, |
| Bourdon | . . | 5·55 | 47·69 | 6·01 | 39·30 | | 7·00 | ,, |
| Camon | . . | 5·59 | 46·11 | 5·99 | 35·97 | 2·63 | 9·40 | ,, |
| Riemenconrt | . . | 1·81 | 12·99 | 2·22 | 19·31 | | 65·01 | ,, |
| Vulcaire | . . | . . | 57·03 | 5·63 | 29·67 | 2·09 | 5·58 | Regnault |
| Loug | . . | . . | 58·09 | 5·93 | 31·37 | | 4·61 | ,, |
| Framont | . . | . . | 57·79 | 6·11 | 30·77 | | 5·33 | ,, |
| Friesland | . . | . . | 57·16 | 5·65 | 33·39 | | 3·80 | Mulder |
| | . . | . . | 59·86 | 5·52 | 33·71 | | 0·91 | ,, |
| Holland | . . | . . | 50·85 | 4·65 | 30·25 | | 14·25 | ,, |
| Rammstein | . . | 16·70 | 62·15 | 6·29 | 27·20 | 1·66 | 2·70 | Walz |
| Steinwenden | . . | 16·00 | 57·50 | 6·90 | 31·81 | 1·75 | 2·04 | ,, |
| Niedermoor | . . | 17·00 | 47·90 | 5·80 | 42·80 | | 3·50 | ,, |
| Prussian | . . | 15·70 to | 50·13 | 4·20 | 31·44 | | 8·92 | Baer |
| | | 21·70 | 55·01 | 5·36 | 35·24 | | 11·17 | ,, |
| Havel | . . | 17·63 | 56·43 | 5·32 | 38·35 | | 9·86 | Jackel |
| | . . | 19·32 | 53·51 | 5·90 | 40·59 | | 6·60 | ,, |
| | . . | 18·89 | 53·31 | 5·31 | 41·38 | | 6·80 | ,, |
| Linum | . . | 31·34 | 59·43 | 5·26 | 35·31 | | 11·99 | ,, |
| Hambnrg | . . | 18·83 | 57·20 | 5·32 | 37·56 | | 2·31 | ,, |
| Bremen | . . | . . | 57·84 | 5·85 | 32·76 | 0·95 | 2·60 | Breuninger |
| | . . | . . | 57·03 | 5·56 | 34·15 | 1·67 | 1·57 | ,, |
| Schopfloch | . . | 20·00 | 53·59 | 5·60 | 30·32 | 2·71 | 8·10 | Nessler and |
| Sindelfingen | . . | 18·00 | 45·44 | 5·28 | 26·21 | 1·46 | 21·60 | Petersen |
| | . . | 18·00 | 38·72 | 4·24 | 25·89 | 0·88 | 30·60 | ,, |
| Baden | . . | 11·77 to | 46·75 | 3·57 | 25 87 | 0·67 | 0·89 | ,, |
| | | 18·55 | 60·79 | 7·10 | 49·01 | 6·33 | 14·76 | ,, |

ANALYSES OF PEAT ASHES.

| Source. | Dutch. | Scotch. | | American. | | Bavarian. | Irish. | |
|---|---|---|---|---|---|---|---|---|
| Authority. | Anderson. | | | Johnson. | | Wagner | Sullivan and Gages | |
| Soda . . . | 1·1 | 1·0 | . . | 0·6 | . . | 0·3 | 0·679 | 1·427 |
| Potash . . | 1·2 | 0·7 | 0·4 | 0·7 | 0·8 | 0·7 | 0·347 | 0·362 |
| Magnesia . . | 4·5 | 0·4 | . . | 6·0 | 4·9 | 0·9 | 1·256 | 3·392 |
| Lime . . | 11·7 | 1·2 | 1·3 | 40·5 | 35·6 | 11·2 | 45·581 | 26·113 |
| Alumina . . | 2·9 | . . | 1·8 | . . | . . | 28·4 | 0·129 | 4·180 |
| Ferric oxide . | 5·3 | 30·7 | 12·5 | 5·1 | 9·1 | 4·5 | 15·974 | 11·591 |
| Phosphoric acid . | . . | . . | . . | 0·5 | 0·7 | 0·9 | 0·188 | 1·461 |
| Sulphuric acid . | 9·7 | 5·5 | 2·0 | 5·5 | 10·4 | 2·6 | 44·371 | 12·403 |
| Chlorine . . | 1·5 | . . | 0·1 | 0·1 | 0·4 | trace | HCl 0·337 | 1·568 |
| Silica . . | 9·8 | . . | 81·6 | 8·2 | 1·4 | 12·3 | 1·043 | 0·980 |
| Carbonic acid . | . . | . . | . . | . . | . . | 1·0 | 16·120 | 13·695 |
| Sand, clay, &c. . | 51·5 | 60·6 | . . | 31·7 | 37·3 | 37·2 | 2·653 | 22·519 |
| | | | | | | | 99·678 | 99·691 |

The chemical nature of the change by which peat has been produced from plant-remains is probably very similar to that by which bituminous minerals have been formed from analogous materials. It consists chiefly in elimination of oxygen and hydrogen in the proportion to form water, also of oxygen and carbon in the proportion to form carbonic acid, and of hydrogen and carbon in the proportion to form marsh gas and perhaps other hydrocarbons, the main feature of this change being the increase in the amount of carbon in the residual substance. Hence the composition of different kinds of peat varies in proportion to the extent to which this alteration may have advanced, and peat which has been little altered will possess a composition more or less approximating to that of ligneous tissue or of wood, while those kinds which have undergone greater alteration will possess a composition approximating more to that of coal, or lignite, or other bituminous minerals, according to the conditions under which this change has taken place. The physical characters of peat, such as texture, colour, density, &c., also bear a similar relation to the degree of chemical alteration which has been reached, the fibrous, light coloured, spongy kinds being most similar to wood in composition as well as most unlike coal or lignite, &c., while on the contrary the compact, dark coloured, dense varieties of peat often resemble lignite and some kinds of coal in composition as well as in their physical characters. It is indeed probable that peat may be regarded as a sort of intermediate product of the same general mode of alteration by which coal and other bituminous minerals have been formed, and that if deposits of peat were placed under conditions such as those in which coal, &c., have been produced, the peat might in process of time become converted into coal.

B. H. P.

**PECTASE.** A fermentative substance existing in fruits, and having the property of converting pectin into pectic, parapectic, and metapectic acids. It has not been obtained in the pure state. (See p. 362.)

**PECTIC ACID.**
**PECTIN.**
} See PECTOUS SUBSTANCES (p. 362).

**PECTOLITE.** *Osmelite.*—A hydrated silicate of calcium and sodium, occurring in aggregated acicular monoclinic crystals, having nearly the same angles as wollastonite, and cleaving perfectly parallel to the orthodiagonal. Twins, parallel to ∞P∞, are of frequent occurrence. It also occurs fibrous, massive, radiated or stellar. Hardness = 5. Specific gravity = 2·68—2·74. Colour whitish or greyish, with silky or subvitreous lustre on the fractured surface; subtranslucent to opaque. Tough like dysclasite. Melts before the blowpipe to a translucent glass. Decomposed by hydrochloric acid, with separation of flocculent silica; gelatinises if previously ignited.

*Analyses.*—*a.* From Monte Baldo in Upper Italy (v. Kobell, Kastn. Arch. xiii. 385; xiv. 341).—*b.* Isle Royal, Lake Superior (Whitney, Sill. Am. J. [2] vii. 434).—*c.* Talisker, Isle of Skye; specific gravity 2·784 (Heddle, Phil. Mag. [4] ix. 248).—*d.* Castle Hill, Edinburgh, associated with wollastonite and prehnite (Heddle and Greg, *loc. cit.*).—*e.* Knockdolian Hill near Ballantra, Ayrshire; specific gravity 2·778 (Heddle and Greg).—*f.* Bergen Hill, New Jersey; mean of three closely agreeing analyses (Whitney, Sill. Am. J. [2] xxix. 205).—*g.* Langban's iron-mine in Wermland, Sweden; in fibres like asbestos, but more compact (Igelström, J. pr. Chem. lxxxi. 396).

| | a. | b. | c. | d. | e. | f. | g. |
|---|---|---|---|---|---|---|---|
| Silica | 51·30 | 53·45 | 53·82 | 53·06 | 53·24 | 54·62 | 52·24 |
| Alumina | 0·90 | 4·94 | 2·73* | 0·75 | 1·00 | | |
| Lime | 33·77 | 31·21 | 29·88 | 33·48 | 32·22 | 32·94 | 33·83 |
| Ferrous oxide<br>Manganous oxide | . . | . . | . . | . . | . . | 1·09 | 1·75 |
| Soda | 8·26 | 7·37 | 9·55 | 9·98 | 9·57 | 8·96 | 8·48† |
| Potash | 1·57 | . . | . . | . . | . . | . . | |
| Water | 3·89 | 2·72 | 3·76 | 3·13 | 3·60 | 2·39‡ | 3·70 |
| | 99·69 | 99·69 | 99·74 | 100·40 | 99·63 | 100·00 | 100·00 |

These analyses may be nearly represented by the formula $(Na^2O.2SiO^2).4(Ca''O.SiO^2).H^2O$ or $(NaHCa''^{2})Si^{2}O^{6}$ or $\left.\begin{matrix}\overset{iv}{Si^2}\\ NaHCa''^{2}\end{matrix}\right\}O^6$, requiring 54·87 per cent. silica, 3·25 lime, 9·20 soda, and 2·68 water. From the last analysis Igelström deduces the formula $3(2M^2O.3SiO^2).Ca''H^2O^2$.

**PECTOSE.**
**PECTOSIC ACID.** } See PECTOUS SUBSTANCES.
**PECTOUS ACID.**

**PECTOUS SUBSTANCES.** *Pectin, Pectic acid, Pectose,* &c. (Vauquelin, Ann. Chim. v. 100; vi. 282; Ann. Ch. Phys. [2] xli. 46.—Braconnot, Ann. Ch. Phys. [2] xxviii. 173; xxx. 96; xlvii. 266; lxxii. 433.—Guibourt, J. Chim. méd. i. 27.—Mulder, J. pr. Chem. xiv. 277; xvi. 246.—Frémy, Ann. Ch. Phys. [3] xxiv. 9. —Souheiran, J. Pharm. [3] xi. 417.—Poumarède and Fignier, J. Pharm. [3] xi. 458; xii. 81.—Chodnew, Ann. Ch. Pharm. li. 356.—Fr. John, N. Br. Arch. xlv. 24, 129.—Gm. xv. 392.—Gerh. ii. 584).—The pulp of fleshy fruits in the unripe state, also fleshy roots and other vegetable organs, contain a substance called pectose, which is insoluble in water, but under the influence of acids and other reagents, is transformed into a soluble substance, pectin, identical with that which exists in ripe fruits and imparts to their juice the property of gelatinising when boiled.

Pectose almost always accompanies cellulose in the tissue of plants, but as it is insoluble in water, alcohol and ether, and is moreover decomposed or altered by most reagents, it has not yet been isolated. It is this substance which gives the hardness to unripe fruits. It is probably isomeric with cellulose, or differs from it only by the elements of water.

Pectin does not exist ready formed in fruits, excepting when they are very ripe. It is formed in fruits from pectose under the influence of heat, its formation being then due to the action of citric and malic acids. The juice expressed from an unripe apple does not contain a trace of pectin, but if it be boiled for a few minutes with the pulp of the fruit, pectin soon appears and gives to the liquid the peculiar viscosity which characterises the juice of all boiled fruits.

Pectin may also be formed by boiling the pulp of carrots or turnips with a slightly acid liquid.

Under the influence of acids or alkalis, pectin is gradually modified, and ultimately transformed into a strongly acid compound called metapectic acid, passing however through a series of intermediate modifications called by Frémy, parapectin, metapectin, pectosic acid, pectic acid, and parapectic acid. The composition of these bodies cannot be regarded as definitely established, as they are uncrystallisable, and it is very difficult to free them completely from mineral substances. It is probable however that they are either isomeric modifications of the same chemical compound, or else differ from one another only by the elements of water.

Pectin undergoes transformation not only when subjected to the action of the above-mentioned chemical reagents, but also in the living plant. According to Frémy, all vegetal tissues which contain pectose (the primary material from which pectin is formed), contain also a kind of ferment called pectase, comparable in its mode of action to the diastase of germinating barley and the emulsin of bitter almonds. It is an uncrystallisable substance, which may be obtained by precipitating the juice of fresh carrots with alcohol. The pectase which was previously soluble then becomes insoluble in water, without however losing its power of acting on pectous substances. When introduced into a solution of pectin, it quickly converts that body into a gelatinous product, insoluble in cold water; this transformation takes place in water at the temperature of about 40°. Pectase immersed in water for two or three days, is decomposed, becomes covered with mould, and is then no longer capable of acting as a pectous ferment; its fermentative action is likewise paralysed by prolonged ebullition.

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* With ferric oxide and magnesia.

† By loss. A direct determination of the water in the mineral dried at 80° gave 2·75—3·03 per cent.

‡ By difference.

Pectase exists in the vegetal organism sometimes in the soluble, sometimes in the insoluble state. Roots like carrots and beet-root contain soluble pectase; their juice in fact induces the pectous fermentation, whereas the juice of apples and other acid fruits has no action upon pectin. In these fruits, the pectase is associated with the insoluble portion of the pulp, so that when the pulp of unripe apples is introduced into a solution of pectin, this solution quickly becomes gelatinous, in consequence of the conversion of the pectin into pectosic and pectous acids. Soluble pectase, as already observed, may be rendered insoluble by precipitation with alcohol.

When a fruit, such as a pear, apple, or plum, is heated in contact with water, it experiences, according to Frémy, the following changes. The acid contained in it, which is usually a mixture of malic and citric acids, first acts upon the pectose and converts it into pectin, part of which remains in the juice, rendering it viscous and masking the acidity of the fruit. In the next place the pectase, acting upon the pectin, produces a certain quantity of pectosic acid which gelatinises on cooling. If the action of the pectase be prolonged, the pectosic acid may be changed into pectic acid. If the fruit is rapidly heated, the pectase likewise coagulates, loses its activity, and no longer acts upon the pectin. When a fruit is boiled, the pectose alone is altered, while the cellulose does not experience any change.

Green fruits, as already observed, do not contain pectin ready formed, but only pectose, the scanty precipitate which their juice yields with alcohol being due to albuminous matter. But as the ripening advances, the fruit gradually loses its hardness, the cells become distended and semi-transparent, and the juice then contains only pectin, which does not precipitate neutral acetate of lead. When the fruit is ripe, the juice becomes gummy and contains a large quantity of pectin, and still more of parapectin, which forms a precipitate with acetate of lead. At this time, the pulp, if carefully washed, does not exhibit any sensible quantity of pectose, this substance having been changed in the process of maturation into pectin and parapectin. Lastly, fruits in the over-ripe state no longer contain a trace of pectin, that substance having been converted into metapectic acid, which is saturated by the potash or lime in the fruit.

It appears then that the gelatinous or pectous constituents of fruit experience during vegetation, transformations identical with those which may be produced in them artificially by the action of acids, water, alkalis, or pectase.

We shall now describe the several bodies of the pectous group, taking them in the order in which they are formed from pectose.

**Pectin.** This substance was discovered by Braconnot. Frémy prepares it by treating the expressed and filtered juice of very ripe pears with oxalic acid to precipitate the dissolved lime, and with tannic acid to precipitate albumin, and mixing the filtrate with alcohol, which precipitates pectin in long threads. These are purified by washing with alcohol, repeated solution in cold water, and precipitation with alcohol, till neither sugar nor organic acid can be detected in the solution.—Braconnot boils the recently expressed juice of ripe apples for a while to coagulate the albumin, precipitates the filtrate with alcohol, and purifies it by repeated solution in water and precipitation with alcohol.—Pounarède and Fignier leave comminuted gentian-roots to soften in warm water, wash them thoroughly with water and very dilute acetic acid, digest the roots thus prepared with very dilute acetic acid at 80°—90° for half or three-quarters of an hour, and precipitate the solution with alcohol of 36°.—Mulder precipitates the expressed and filtered juice of apples with alcohol, and boils the precipitate with alcohol, to remove sugar, malic acid and tannin.—Chodnew obtained pectin: α. By boiling crushed pears with water, precipitating the filtered juice with alcohol, and washing with alcohol and ether; whereupon it becomes opaque and acquires the texture of woody fibre. (This pectin is not precipitated by chloride of barium, but gives a precipitate with neutral acetate of lead and sulphate of copper, and therefore agrees with Frémy's parapectin, p. 364);—or β. By boiling the expressed juice of apples, precipitating with alcohol, redissolving in water, mixing the solution with hydrochloric acid, and again precipitating with alcohol. (This pectin resembles the former, but has a slight acid reaction, and sometimes reduces an alkaline cupric solution.)

Stüde (Ann. Ch. Pharm. cxxxi. 58) prepares pectin from radishes, by rasping the pulp, leaving it to macerate for some hours with water, pressing, heating just to the boiling point, filtering, then precipitating with basic acetate of lead, decomposing the precipitate with sulphydric acid, and precipitating the filtrate with alcohol.* He is of opinion that the body which yields pectin when unripe fruits, &c., are boiled with acids, is not a simple proximate principle (pectose), but a compound of pectin with lime; for, on washing radish-pulp completely with water and then treating it with an acid, lime passes into solution as well as pectin.

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* If neutral acetate of lead be added to the boiled solution instead of the basic acetate, a less abundant precipitate is obtained, consisting of lead-sulphate and the lead-compound of a new glycogenous substance.

*Properties.*—Pectin is a white amorphous mass, soluble in water, neutral to test-papers, precipitated by alcohol as a jelly from dilute solutions, in long threads from strong solutions. When pure it is not precipitated by neutral acetate of lead, but it is generally mixed with a certain quantity of parapectin, which gives a precipitate with that reagent. With basic acetate of lead it gives a copious precipitate. It has no action on polarised light. When burnt it emits an odour like that of tartaric acid.

The following are the results of the analyses of pectin prepared in various ways, deducting the mineral substances with which pectin is always contaminated, in whatever way it may be prepared:

| | Mulder. | | Chodnew. | | Frémy. | | | Poumarède & Figuier. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *e.* | *e.* | *f.* | *g.* | *h.* |
| Carbon . . | 44·0 | 45·2 | 46·0 | 43·8 | 39·7 | 39·5 | 40·5 | 43·8 | 43·2 | 43·3 |
| Hydrogen . . | 5·4 | 5·5 | 5·5 | 5·5 | 5 5 | 5·6 | 5·5 | 5·9 | 5·6 | 5·6 |
| Oxygen . . | 50·0 | 49·3 | 48·5 | 50·7 | 54·8 | 54·9 | 54·0 | 50 3 | 51·2 | 51·1 |
| | 100 0 | 100·0 | 100·0 | 100·0 | 100·0 | 100 0 | 100·0 | 100·0 | 100·0 | 100·0 |

*a.* Pectin from sweet apples at 120°, leaving 5·9 per cent. ash, consisting of nearly pure lime, with a little silica and iron oxide.—*b.* Pectin of sour apples at 120°, leaving 9·3 per cent. ash.—*c.* Mean of two analyses of pectin from pears at 115°; it contained 8·5 per cent. ash, composed of lime, magnesia, iron-oxide, potash, chlorine, sulphuric acid and phosphoric acid.—*d.* Pectin of apples at 115°, leaving 1·59 per cent. ash, containing much ferric phosphate without a trace of carbonic acid.—*e.* Pectin of ripe pears. *f.* Mean of three analyses of pectin from gentian dried at 120°, and still containing mineral substances.—*g.* Mean of two analyses of pectin from gentian dried at 120°, and freed from the greater portion of metallic oxide by treatment with alkalis and acids.—*h.* Pectin from carrots dried at 120°.

The preceding analyses, though they agree pretty nearly in the amount of hydrogen, yet differ so greatly in the carbon that it is impossible to represent them by any one formula. The discrepancy doubtless arises from the great difficulty of completely purifying pectin from albuminous substances, sugar, dextrin, malate of calcium, &c., which adhere to it obstinately. The best mode of testing its purity is to precipitate the aqueous solution with excess of baryta-water, which throws down the pectin, leaving the substances just mentioned in solution; if then the liquid filtered from the precipitate and freed from excess of baryta by carbonic acid, leaves no residue on evaporation, it may be presumed that the pectin is pure (Frémy). In the preparation and purification of pectin it is indispensable also, according to Frémy, to avoid the use of boiling water, which alters it rapidly by converting it into parapectin. Frémy deduces from his own analyses of pectin the formula $C^{32}H^{48}O^{32}$, requiring 40·7 per cent. carbon, 5·1 hydrogen, and 54·2 oxygen.

*Decompositions.*—Boiling *water*, as already observed, converts pectin into parapectin. *Dilute acids* at the boiling heat convert it into metapectin, and finally into metapectic acid. *Alkalis* and *alkaline earths* immediately change it into pectates, and these salts when treated with acids yield insoluble pectic acid. Lastly, under the influence of *pectase*, pectin is converted into pectosic acid.

**Parapectin.** Aqueous pectin, when boiled for several hours, loses its gummy consistence, and is converted into parapectin, which is precipitated by alcohol in the form of a translucent jelly. It then still retains albuminous substances, which are precipitated from the aqueous solution by addition of a small quantity of basic acetate of lead.

Parapectin is an amorphous, neutral substance resembling pectin; tasteless; soluble in water, like pectin and metapectin; distinguished from the former by being precipitable by neutral acetate of lead, and from the latter by not being precipitated by chloride of barium. It is isomeric with pectin at 100°, but gives up 1 at. water when heated to 140°.

| | at 140°. | | Frémy. *a.* | *b.* | *c.* |
|---|---|---|---|---|---|
| $C^{32}$ | 384 | 41·48 | 41·51 | 42·88 | 43·77 |
| $H^{46}$ | 46 | 4·97 | 5·48 | 5·68 | 5·41 |
| $O^{31}$ | 496 | 53·55 | 53·01 | 51·44 | 50·82 |
| $C^{32}H^{46}O^{31}$ | 926 | 100·00 | 100·00 | 100·00 | 100·00 |

*a* is parapectin several times purified; *b* and *c* are less pure.

Parapectin is converted, by boiling with dilute *acids*, into metapectin; by aqueous *alkalis* into a salt of pectic acid. Its aqueous solution precipitates *neutral acetate of lead*, forming a precipitate containing very variable quantities of lead-oxide (from 11·9 to 18·8 and 21·2 per cent.). The organic portion of the precipitate was found to contain 41·95 per cent. carbon, and 5·42 hydrogen. (Frémy.)

**Metapectin.** $C^{32}H^{46}O^{31}$?—Parapectin is quickly converted into this substance by boiling with dilute acids. It is uncrystallisable; has an acid reaction; is soluble in water, like pectin and parapectin; distinguished from both by its acid properties and precipitability by chloride of barium. Metapectin dried at 100°, gives off 1 at. water at 140°, and then exhibits the same composition as parapectin (by analysis, 41·85 per cent. carbon, and 5·58 hydrogen).

By *alkalis* it is converted into a salt of pectic acid. It dissolves in *water;* if the solution also contains hydrochloric, sulphuric, or oxalic acid, alcohol throws down gelatinous compounds of these acids with metapectin. From aqueous metapectin, *chloride of barium* throws down a precipitate containing from 14 to 15 per cent. baryta ($C^{32}H^{46}O^{31}Ba''O$ = 14·1 per cent. baryta). The *lead-compound* contains 19·43 per cent. lead-oxide ($C^{32}H^{46}O^{31}.Pb''O$ = 20·30 per cent. $Pb''O$).

**Pectosic acid.** This acid, probably isomeric with parapectin and metapectin, is obtained as the first product of the action of pectase or of aqueous alkalis on aqueous pectin the solution solidifying to a jelly immediately or after addition of acids; but it is quickly converted into pectic acid by the further action of the same agents, or by boiling water. It has an acid reaction; is nearly insoluble in cold *water*, quite insoluble in water containing hydrochloric acid, but easily soluble in boiling water (whereby it is distinguished from pectin), and forms a jelly on cooling. It gave by analysis 41·1 per cent. carbon, and 5·25 hydrogen. (Frémy.)

The gelatinous amorphous *pectosates* are easily converted into pectates by excess of base; when pure they dissolve completely in warm dilute acid, whereas pectates leave a residue of pectic acid.

The *barium-salt* precipitated from aqueous pectin by a quantity of baryta-water insufficient for complete precipitation, contains, on the average, 24·4 per cent. baryta ($C^{32}H^{44}Ba''O^{31}$ = 25·3 per cent. BaO).

The *lead-salt* contains 32·75 per cent. lead-oxide, the formula $C^{32}H^{44}Pb''O^{31}$ requiring 33·42 per cent. PbO.

**Pectic acid.** $C^{16}H^{22}O^{15}$?—This acid, though it may be obtained from most plants, if not from all, does not exist in them ready formed, at least not always, but is produced from pectose or pectin. In fact when a solution of pectin holding potash in suspension is left to itself at a temperature of 30°, the pectin is first converted into pectosic, then into pectic acid. Dilute solutions of potash, soda, alkaline carbonates, ammonia, and aqueous baryta, strontia, and lime, transform pectin almost immediately into pectates. Pectic acid is extracted from its different salts by submitting pectates to the action of acids.

*Preparation.*—1. Well washed carrot-pulp is boiled with water slightly acidulated with hydrochloric acid, whereby pectin is dissolved. This pectin is converted into pectate of sodium by boiling with the proper quantity of sodic carbonate (to be determined by trial); the solution is precipitated with hydrochloric acid; and the separated pectic acid is dried, first in vacuo, then by heat. If too small a quantity of carbonate is added, pectosic acid may be formed; if too much, metapectic acid may be produced (Frémy).—2. The pulp of peeled turnips is well washed with water and pressed, and the residue is boiled for three quarters of an hour with water to which $\frac{1}{10}$ of sodic carbonate, or a small quantity of caustic potash, has been added. The liquid is filtered, the solution is precipitated with chloride of calcium; and the pectate of calcium is decomposed by hydrochloric acid (Braconnot, Regnault; Simouin, J. Pharm. xx. 478. Regnault dissolves the still coloured pectic acid in aqueous ammonia; decolorises it with animal charcoal at 60° to 80°; precipitates the filtrate with hydrochloric acid; and repeats the solution in ammonia and precipitation with acid, in order to remove the mineral constituents.

3. The pulp of carrots or celery is exhausted by washing with pure water, boiling with water containing hydrochloric acid, and again washing with pure water; the residue is boiled with very dilute potash-ley; and the solution is precipitated by hydrochloric acid (Braconnot). Frémy obtained by this process only a small quantity of pectic acid (*vid. sup.*). Chodnew boils turnips after trituration, washing and pressing, with very dilute potash, for half to three quarters of an hour; strains; precipitates the still turbid solution with hydrochloric acid; washes the pectic acid several times, first with acidulated, then with pure water; presses it with the hand after each washing, and redissolves it in ammonia, whereby an easily filtering liquid is obtained, which, after filtration, is precipitated by hydrochloric acid. This precipitate is washed as above, and finally with alcohol.*

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* By boiling the washed pulp of turnips or apples with hydrochloric acid, precipitating with alcohol, then washing the precipitate with alcohol or ether, pressing and drying at 120°, Chodnew obtained a non-friable mass like woody-fibre, which he calls pectous acid; it is slightly acid, soluble in water even after drying, precipitated as a jelly by excess of potash or lime-water, but not by chloride of po-

According to **Frémy**, pectic acid prepared in the ordinary way (probably according to methods 2 and 3) contains albuminous substances which may be more easily precipitated by small quantities of basic acetate of lead, after prolonged boiling of the solution supersaturated with ammonia.

**Mulder** washes comminuted carrots, turnips or sweet apples with water, boils the residue with very dilute potash, not in excess, and precipitates with hydrochloric acid.

**Fromberg** prepared his pectic acid from turnips by comminution, washing with cold water, and boiling with very dilute carbonate of sodium.

According to **Divers** (Chem. Soc. J. xvii. 91) pectic acid is produced, together with parapectic acid, by the spontaneous decomposition of gum cotton.

*Properties.*—Pectic acid in the moist state, is a transparent, colourless jelly, which dries up to a white, transparent, horny mass, difficult to pulverise. It has an acid taste and reaction. It is insoluble in cold, nearly insoluble in boiling water, insoluble also in alcohol and in ether. Its composition is as follows:—

| | *Calculation* (Frémy). | | Mulder. *a.* | *b.* | Fromberg. | Regnault. at 140°. | Chodnew. at 120° | Frémy. at 120°. |
|---|---|---|---|---|---|---|---|---|
| $C^{16}$ | 192 | 42·29 | 44·9 | 44·6 | 44·5 | 42·69 | 42·22 | 41·40 |
| $H^{22}$ | 22 | 4·84 | 5·4 | 5·3 | 5·2 | 4·71 | 5·24 | 4·77 |
| $O^{15}$ | 240 | 52·87 | 49·7 | 50·1 | 50·3 | 52·60 | 52·54 | 53·83 |
| $C^{16}H^{22}O^{15}$ | 454 | 100·00 | 100·0 | 100·0 | 100·0 | 100·00 | 100·00 | 100·00 |

The analyses are given as mean results. Regnault and Chodnew examined pectic acid prepared from turnips; Frémy analysed acid from various sources. Chodnew's acid left ½ per cent. ash, which is deducted: see above. Mulder's pectic acid *a* was obtained from carrots, and left 4·17 per cent. of ash, composed of lime with traces of silica; *b* was obtained from sweet apples, and left 3·2 per cent. ash. Fromberg's pectic acid, obtained from turnips and dried at 140°, left 7 per cent. ash, composed in great part of caustic lime.

The analyses of pectic acid differ from one another as widely as those of pectin. It is most probable, however, that pectic acid, as indicated by Frémy's formula, differs from pectin only by the elements of water. Regnault gave the formula $C^{11}H^{14}O^{10}$, both for pectic acid dried at 140°, and for that contained in the salts. Chodnew gives the formula $C^{14}H^{20}O^{13}$, which agrees with the composition of many of the pectates, and requires 42·42 per cent. carbon, 5·06 hydrogen, and 52·52 oxygen.

*Decompositions.*—1. Pectic acid becomes coloured at 120° (**Regnault**); black at 150° (**Chodnew**), and at 200° gives off carbonic anhydride and water, and is converted into parapectic acid, p. 368 (**Frémy**).—2. It melts when heated, swells up, burns away, and leaves a difficultly combustible charcoal (**Regnault**).—3. When pectic acid is boiled with *water*, parapectic acid is formed; likewise when insoluble pectactes are boiled with water (**Frémy**). When pectic acid is left in contact with water for two or three months, it dissolves as metapectic acid, which is likewise produced when pectic acid is boiled with water for 36 hours, or when moist pectic acid is dried by heat. Not a trace of sugar is formed, even after boiling with water for seven or eight days, and the solution does not reduce potassio-cupric tartrate unless it contains para- or metapectic acid (**Frémy**). See below.

4. Pectic acid is not altered by cold *oil of vitriol*, but is quickly charred by that liquid when heated (**Braconnot**, **Regnault**). By boiling with *dilute acids*, it is converted into metapectic acid, which dissolves (**Fremy**). It is not altered by hot very dilute *hydrochloric acid* (**Regnault**).—Pectic acid prepared from turnips does not dissolve till after very long boiling with dilute acids (more quickly with concentrated acids) and the solution does not contain metapectic acid; that which is prepared from pectin decomposes much more quickly. When the first-mentioned pectic acid is boiled with dilute mineral acids, the liquid soon acquires a faint red colour, reduces copper- and silver-salts, and if sulphuric acid is used, gives off carbonic and formic acids, and, finally, an odour of caramel. The solution, which remains colourless if diluted at the right moment, leaves a black product when filtered, and if evaporated after the sulphuric acid has been removed by carbonate of barium, it leaves a syrup from which alcohol precipitates a barium-salt soluble in water, leaving in solution a sugar (partly converted into caramel), which is fermentable and capable of uniting with common salt. The barium-salt, which is soluble in water, appears to contain formic

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tassium; converted into pectic acid by solution in potash-ley and precipitation with hydrochloric acid; contains 43·2 per cent. carbon, 5·6 hydrogen, and 51·2 oxygen.

Another acid, called **hyperpectic acid**, is obtained from the turnip-pulp after exhaustion with hydrochloric acid, by boiling it with dilute potash (not with ammonia), and precipitating with hydrochloric acid. It is a gelatinous substance, containing (at 100°) after deduction of 0·52 per cent. ash, 41·5 per cent. carbon, 4·8 hydrogen, and 53·7 oxygen, and is distinguished from pectic acid by not dissolving in ammonia. (**Chodnew**.)

acid, and an acid similar to malic acid (Chodnew). The jelly of pippins completely freed from sugar by alcohol, is converted into sugar by twenty minutes boiling with oxalic acid (Couverchel, Ann. Ch. Phys. [2] xlvi. 181). According to Frémy, pectic acid is transformed by acids in the same manner as by water, therefore without formation of sugar. Frémy attributes the formation of sugar in Chodnew's experiments to the presence of starch in the pectic acid employed.

5. With *nitric acid*, pectic acid yields oxalic acid (Vauquelin) and mucic acid (Braconnot). Chodnew obtained mucic acid from pectin, but not from pectic acid.

When pectic acid is heated with the aqueous solution of *caustic alkalis* or *alkaline carbonates*, metapectic acid is formed (Frémy). Pectin and pectic acid prepared from it, undergo these transformations much more readily than ordinary pectic acid (Frémy, Chodnew). The liquid acquires a brown colour, but is not found to contain oxalic acid (Frémy).

*Pectates.* The pectates of the alkali-metals are soluble in water, the rest insoluble and gelatinous. The jellies precipitated from cold solutions are denser than those obtained from hot solutions (Regnault). At a moderate heat, the acid expels carbonic acid from alkaline carbonates. It dissolves easily in aqueous alkalis, even after drying. The solution is not precipitated by mercuric chloride, but with all other salts it yields gelatinous precipitates, which dissolve in excess of alkali. It is difficult to obtain the salts at a definite degree of saturation, because the neutral salts formed at first take up an additional quantity of pectic acid (Regnault, Frémy). When a soluble pectate is precipitated by a metallic salt, the composition of the precipitate depends upon that of the soluble salt, and varies with it (Regnault). The jellies precipitated by metallic salts from pectate of ammonium and pectate of calcium, are transparent if the acid was pure. They obstinately retain portions of the precipitant, which cannot be removed by washing on the filter, but may be got rid of by pressing the jelly with the hand, pouring fresh water upon it, and so on, whereby the salt acquires the consistence of woody fibre, and becomes friable after drying (Chodnew). The insoluble salts dry up to very hard, difficultly friable, horny, hygroscopic masses. They take fire when heated in contact with the air, retain water obstinately, so that they cannot be dried below 140° or 150°, and decompose at about 200° (Regnault).

The *ammonium-salt* is obtained as a colourless jelly by dissolving pectic acid in ammonia, and precipitating with alcohol.—The *potassium-salt* is obtained in like manner as a jelly which becomes fibrous when washed with alcohol and dried at 120°. It redissolves in water forming a neutral solution. Chodnew found 18·89 per cent. potash ($K^2O$) in the salt dried at 120°, and 20·0 per cent. in the salt dried between 150° and 160°.—The *sodium-salt* obtained in like manner is a colourless jelly containing (at 120°) 13·73 per cent. sodium. (Chodnew.)

*Pectate of barium* is obtained as a colourless jelly by mixing chloride of barium with a solution of pectic acid in ammonia. Frémy obtains it pure by treating a cold solution of pectin protected from the air with a large excess of baryta-water. A copious precipitate of pectosate of barium is then formed, which changes into pectate under the influence of excess of base. The precipitate is to be quickly washed and dried, first in a vacuum, then in a stove at 120°. It contains 20·1 per cent. baryta. (Mulder.)

The *calcium-salt* is obtained in like manner as a transparent jelly, which in three preparations, dried at 120°, gave 12·38, 12·42, and 12·46 per cent. lime. (Chodnew.)

The *copper-salt* is a green jelly containing 16·86—16·38 per cent. cupric oxide (Chodnew); of variable composition (Regnault). The *lead-salt* obtained by precipitating acetate of lead with an ammoniacal solution of pectic acid, contains very variable quantities of pectic acid (34 to 60 per cent. according to Frémy). The organic matter in this precipitate contains, according to various analysts, from 42·9 to 45·2 per cent. carbon, 5·2 to 4·5 hydrogen, and 49·6 to 53·0 oxygen. The *silver-salt* is difficult to obtain pure. Regnault found it to contain quantities of silver-oxide varying from 37·7 to 41·0 per cent.

From the above discordant results of the analyses of pectates, it is impossible to obtain any verification of the formula of pectic acid.

**Parapectic acid.** $C^{24}H^{34}O^{23}$?—Pectic acid boiled for some time with water dissolves as parapectic acid. In like manner, pectates heated for several hours to 150° or boiled with water, are converted into parapectates. Parapectic acid is also formed, together with pectic acid, by the spontaneous decomposition of gun-cotton. (Divers, Chem. Soc. J. xvii. 91.)

Parapectic acid is soluble in water, uncrystallisable, destitute of optical rotatory power, and has a strong acid reaction. When *heated*, it behaves like pectin; when dissolved in *water*, it is quickly converted into metapectic acid; when boiled with *potassio-cupric tartrate*, it precipitates cuprous oxide; and it is not fermentable.—It forms soluble salts with the *alkalis*, and is precipitated therefrom by excess of *baryta-water*, being thereby distinguished from metapectic acid; from its aqueous solution it is precipitated by alcohol. The *potassium-salt* precipitated from its aqueous solution by alcohol, and dried at 150°, contains 23 per cent. potash ($C^{24}H^{30}K^4O^{23}$ = 22·4 per cent. $K^2O$).—The *lead-salt* obtained by boiling pectate of lead suspended in water for several hours, or by precipitating aqueous parapectic acid with neutral acetate of lead, was found to contain from 40·0 to 41·7 per cent. lead-oxide, and the organic part of the precipitate gave, as the mean of three analyses, 43·9 per cent. carbon and 4·7 hydrogen, whence Frémy deduces the formula $C^{24}H^{30}Pb^2O^{23}$.

**Metapectic acid.** $C^8H^{14}O^9$? *Acide cellulique.*—This acid occurs as a product of the transformation of pectose, in all fluids of the vegetable organism which are in contact with tissue containing pectase. All pectous substances may be converted either directly into metapectic acid, or into products which yield this acid after further treatment. When lime is allowed to act on mangold-wurzel pulp in the manufacture of sugar on the large scale, metapectate of calcium may be formed, which then accumulates in the molasses. It may be prepared by washing chopped mangold-wurzel with water; boiling the residue for an hour with milk of lime and pressing; evaporating the liquid to a syrup, and mixing it with alcohol. Metapectate of calcium then falls to the bottom, and after it has been decomposed by oxalate of ammonium, the filtered solution is mixed with excess of neutral acetate of lead to precipitate colouring matter, phosphoric acid and other substances; and the filtrate is supersaturated with ammonia, which throws down metapectate of lead. By decomposing this salt under water with sulphydric acid, and evaporating the filtrate, aqueous metapectic acid is obtained as an amorphous, strongly acid mass, destitute of rotatory power, deliquescent, and easily soluble in water. The aqueous solution quickly becomes covered with mould, and is decomposed by prolonged boiling, with formation of acetic acid and black ulmic acid. It reduces *potassio-cupric tartrate* at the boiling heat, also *silver* and *gold salts*. The *metapectates* (excepting the basic salts) are all soluble in water. The aqueous acid decomposes carbonates and neutralises strong bases.

*Metapectate of Lead.*—Aqueous metapectic acid precipitates basic acetate of lead, but not the neutral acetate. The aqueous solutions of the alkaline metapectates added to neutral or basic acetate of lead in excess (of the lead-salt?) throw down soluble precipitates. The precipitates thrown down from aqueous metapectic acid by basic acetate of lead contain from 67·5 to 68·8 per cent. ($C^8H^{10}Pb^2O^9$ = 67·2 per cent. PbO) and 73·4 to 74·2 per cent. oxide of lead ($C^8H^{10}PbO^9.Pb''O$ = 75·4 per cent. PbO); after deduction of the lead-oxide, they contain on the average 43·51 per cent. C, 4·58 H, and 5·91 O, corresponding to the formula $C^8H^{10}O^7$ (calc. 44·08 per cent. C, 4·58 H, and 51·3 O).

**Pyropectic acid.** When pectin or either of its derivatives, such as pectic, parapectic, or metapectic acid, is heated to 200°, water and carbonic anhydride are evolved, and pyropectic acid remains in the form of a black substance insoluble in water, but soluble in alkaline liquids. It contains 51·3 per cent. carbon, 5·3 hydrogen, and 43·4 oxygen, whence Frémy deduces the formula $C^{14}H^{18}O^9$. It is remarkable that the hydrogen and oxygen in this body are in the same proportion as in the black acid of sugar.—Pyropectic acid forms brown uncrystallisable salts. (Frémy.)

### *General view of the transformations of Pectin and the mutual relations of Pectous substances.*

1. *Pectose* heated with dilute acids is converted into pectin, which by longer boiling is transformed into metapectic acid.

2. By boiling with milk of lime, it is converted into metapectic acid. Probably pectic acid is formed in the first instance.

3. *Pectin*, when its aqueous solution is left to itself, changes into metapectic acid. If pectase is likewise present, the change takes place more quickly, pectosic, pectic, and metapectic acid being successively produced. When pectin is boiled with water, parapectin is produced.

4. Pectin boiled with strong acids, is converted into metapectic acid.

5. By cold dilute aqueous alkalis, it is converted into pectosic acid, which quickly undergoes further transformation into pectic acid, or by boiling with strong alkalis, into metapectic acid.

6. *Parapectin* boiled with dilute acids is converted into metapectin; aqueous alkalis convert it into a pectate.

7. *Metapectin* is converted by alkalis into salts of pectic acid.

8. *Pectosic acid* is converted into pectic acid by boiling with water, either pure or alkaline, or by contact with pectose. When boiled with aqueous alkalis it forms metapectic acid.

9. *Pectic acid* is converted, by long contact with water in the cold, more quickly at

the boiling heat, into parapectic acid, then further into metapectic acid. Boiling with acids or alkalis likewise converts it into metapectic acid.

10. *Parapectic acid* in contact with water, is quickly converted into metapectic acid.

11. *Metapectic acid* cannot be converted into any other substance of the pectin group.

**PEGANITE.** Native phosphate of aluminium from Strigis near Freiberg (see PHOSPHATES).

**PEGANUM HARMALA, ALKALOÏDS OF.** See HARMALINE and HARMINE (iii. 7).

**PEGMATITE.** Graphic granite.

**PEGMATOLITE.** Syn. with ORTHOCLASE.

**PEGMIN.** A protein-substance obtained by Thomson from the buff coat of the blood of men and horses, by washing with cold water and exhausting the dried residue with alcohol and ether. It contains sulphur, and is regarded by Thomson as a peculiar substance.

**PELARGONE.** $C^{17}H^{34}O = C^8H^{17}.C^9H^{17}O$. *Octyl-pelargyl.*—When pelargonate of barium is submitted to dry distillation, this compound passes over as a brown oil which solidifies on cooling, while carbonate of barium remains behind. The distilled products, after pressure between bibulous paper, form a solid substance which dissolves easily in ether, and is deposited by spontaneous evaporation in large laminæ which assume a nacreous aspect when dry. It is strongly attacked by fuming nitric acid, forming a nitro-acid.

**PELARGONENE.** $C^9H^{18}$. Syn. with NONYLENE (p. 134).

**PELARGONIC ACID.** $C^9H^{18}O^2 = \left.\begin{matrix}C^9H^{17}O\\H\end{matrix}\right\}O$. (Redtenbacher [1846], Ann. Ch. Pharm. lix. 52.—Pless, *ibid.* lix. 54.—Gerhardt, Ann. Ch. Phys. [3] xxiv. 107. —Cahours, Compt. rend. xxvi. 262.—Chiozza, Ann. Ch. Phys. [3] xxxix. 207).—This acid exists in the volatile oil of *Pelargonium roseum.* 1. It is produced, together with several other volatile acids, in the distillation of choloidic and of oleic acid (p. 193), with nitric acid (Redtenbacher).—2. In the oxidation of oil of rue by nitric acid (Gerhardt and Cahours).—3. A small quantity of pelargonic acid is formed together with many other volatile acids, in the putrefaction of yeast. (W. Muller, J. pr. Chem. lxx. 66; O. Hesse, *ibid.* lxxi. 472.)

*Preparation. From oil of rue.*—When 1 pt. of oil of rue is gently heated with 1 pt. of commercial nitric acid and 2 pts. of water, an action sets in, violent at first and continuing for a quarter or half an hour, even after the fire has been removed. The liquid is then boiled and cohobated repeatedly, till scarcely any red fumes are evolved; the layer of oil is decanted, washed with water, and treated with aqueous potash, whereupon some non-acid oil of a very acrid odour is separated; the alkaline solution is decomposed by sulphuric acid; and the oily acid which separates, and is contaminated with resin and colouring matters, is collected and rectified. The distillate is neutralised with baryta, freed from excess of baryta by cold water, dissolved in boiling alcohol, then filtered and cooled to the crystallising point. Pelargonate of barium then crystallises out (the mother-liquor sometimes retains caprate of barium); and this salt decomposed by dilute sulphuric acid yields pelargonic acid, as an oil floating on the surface (Gerhardt). Owing to certain circumstances not ascertained, a compound of nitric oxide with pelargonic acid is sometimes obtained in this process. (Chiozza.)

*From the blossom and herb of Pelargonium roseum.*—The herb is distilled with water; the distillate saturated with baryta; the neutral oil distilled off; and the residue evaporated to dryness and exhausted with boiling alcohol, which takes up pelargonate of barium. (Pless.)

*Properties.*—Pelargonic acid is a colourless oil (greasy according to Redtenbacher) which solidifies in the cold, melting afterwards at 10°. Smells slightly of butyric acid. Boils at 260°; in a stream of carbonic anhydride it distils undecomposed and colourless (Cahours). It is slightly soluble in water, very soluble in alcohol and ether.

*Decompositions.*—1. Pelargonic acid becomes yellow by keeping (Cahours).—2. When 1 pt. of pelargonic acid is intimately mixed with 4 pts. of *potash-lime*, and gradually raised to a red heat in a coated retort, much gas escapes, a clear, amber-yellow, thin liquid passes over, and the alkali, partly combined with carbonic acid, remains behind. Bromine absorbs the greater part of the gas, composed of ethylene, tritylene and tetrylene; the uncondensed portion burns with a very faint flame, and is a mixture of hydrogen and marsh-gas. The liquid, during rectification, begins to boil at 105° to 186°; up to 110° hexylene passes over; the remainder between 135° and 140° (Cahours).—3. The acid is resolved by the dry distillation of its barium-salt

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into carbonic anhydride and pelargone (Cahours).—4. It is violently acted upon by *pentachloride of phosphorus*, evolving hydrochloric acid and forming oxychloride of phosphorus and chloride of pelargyl. (Cahours.)

*Pelargonate of Ammonium* is crystalline (Cahours). Pelargonic acid suspended in ammonia and heated forms a transparent jelly, resembling gelatinous silica. This jelly dissolves when heated with a larger quantity of water, and forms a milky liquid, resembling a solution of soap, and congealing in the cold to a pap-like jelly. The salt dissolves very readily in cold alcohol (Gerhardt). The *potassium-* and *sodium-salts* are readily soluble and crystallisable. (Cahours.)

*Pelargonate of Barium*, $C^{18}H^{34}Ba''O^4$, prepared as above. forms white scales, having a pearly lustre (Gerhardt); large laminæ resembling cholesterin (Redtenbacher). Contains no water of crystallisation. Dissolves but sparingly in cold, somewhat more in hot water (Gerhardt); dissolves in water less readily than the similarly crystallising valerate and œnanthylate of barium, but more readily than the caprate. It dissolves with difficulty in alcohol (Redtenbacher). The *calcium-* and *strontium-salts* crystallise from alcohol in pearly scales, sparingly soluble in water.

*Pelargonate of Copper*, $C^{18}H^{34}Cu''O^4$, is obtained by precipitating the alcoholic ammonium-salt with aqueous nitrate of copper. The abundant greenish-blue precipitate dissolves in boiling alcohol, and on evaporation yields drops of a green oil which solidify on cooling, and when dissolved in boiling alcohol crystallise in greenish-blue grains as the liquid cools. It retains 2 at. water at 100°, and in that state gives by analysis 15·45 per cent. of copper (calc. 15·38).

*Pelargonate of Silver*, $C^9H^{17}AgO^2$, is obtained by precipitating the hot aqueous solution of the barium-salt with nitrate of silver. Analysis 40·7—41·16 per cent. silver—calc. 40·75 per cent.

*Pelargonate of Ethyl.* $C^{11}H^{22}O^2 = C^9H^{17}(C^2H^5)O^2$. *Pelargonic ether.*—Produced from chloride of pelargyl and alcohol; also by passing dry hydrochloric acid gas through alcoholic pelargonic acid, whereupon the ether separates as a yellow oil, which is to be washed successively with sodic carbonate and water, then dried over chloride of calcium and rectified. When thus purified it forms a colourless oil of specific gravity 0·86, boiling between 216° and 218°. By boiling with potash it is resolved into alcohol and pelargonate of potassium. The so-called *œnanthic ether* (p. 174) is probably the same compound.

**PELARGONIC ANHYDRIDE.** $C^{18}H^{34}O^3 = (C^9H^{17}O)^2O$.—*Anhydrous Pelargonic acid. Pelargonic Pelargonate.* (Cahours, Ann. Ch. Phys. [3] xxxix. 207.)—Obtained by the action of oxychloride of phosphorus on pelargonate of barium. Colourless oil, lighter than water, solidifying at 0° to a mass of fine needles, which melts at 5°. Smells slightly rancid in the cold, but vinous and aromatic when mixed with hot aqueous vapour. Heated on glass, it evolves acrid fumes and the odour of burnt fat. It is very slowly transformed into pelargonic acid by water; by aqueous alkalis less easily than caprylic anhydride.

*Benzopelargonic Anhydride*, $C^{16}H^{22}O^3 = \left.\begin{matrix}C^9H^{17}O\\ C^7H^5O\end{matrix}\right\}O$. Already described (i. 558).

**PELARGONIC ETHER.** See PELARGONATE OF ETHYL (*supra*).

**PELARGYL.** $C^9H^{17}O$.—The radicle of pelargonic acid, &c.

*Chloride of Pelargyl*, $C^9H^{17}OCl$, is obtained by the action of pentachloride of phosphorus on pelargonic acid. After rectification it forms a colourless liquid heavier than water, having a suffocating odour, giving off dense fumes on exposure to the air, and boiling at 220°. In contact with alcohol it becomes strongly heated, and forms pelargonate of ethyl. (Cahours, *loc. cit.*)

**PELE'S HAIR.** A capillary variety of obsidian from Hawaii (p. 170).

**PELICANITE.** A variety of cimolite (i. 985) from the decomposed granite of Kiew in Russia.

**PELIOM.** A smoky-blue variety of dichroite from Bodenmais in Bavaria (ii. 320).

**PELLUTEINE.** A base formed, according to Bödeker, from hydrated pelosine, by contact with air and light. On treating the yellow product with alcohol, pelluteine dissolves and separates on cooling in brownish-yellow flocks, containing (at 110°) 73·9 per cent. carbon, 6·2 hydrogen, and 3·8 nitrogen, agreeing approximately with the formula $C^{15}H^{19}NO^3$. The *chloroplatinate* is a precipitate containing from 17·7 to 18·0 per cent. platinum.

**PELOCONITE.** A variety of cupreous manganese (iii. 814), having a liver-brown streak.

**PELOPIUM.** See NIOBIUM (p. 48).

**PELOSINE** or *Cissampeline*. $C^{18}H^{21}NO^3$. (Wiggers, Ann. Ch. Pharm. xxvii. 29;

xxxiii. 81. Bödeker, lxix. 53.)—An alkaloïd contained in the root of *Pareira brava*, commonly attributed to *Cissampelos pareira*, L., a shrubby menispermaceous plant, growing chiefly on the woody hills of the Antilles. It is obtained by exhausting the root with dilute sulphuric acid, precipitating with carbonate of sodium (not in excess), dissolving the precipitate in ether, and evaporating. Pareira root yields from $\frac{1}{25}$ to $\frac{1}{20}$ of its weight of pelosine.

Pelosine obtained as above forms an amorphous transparent varnish. On adding water to the ethereal solution, and expelling the ether by distillation, it separates as a white pulverulent hydrate, which gives off its water at 100°, and leaves a residue soluble in alcohol and ether. Pelosine is insoluble in water, uncrystallisable, inodorous, but has a sweetish bitter taste. It blues reddened litmus. When dried at 120° it contains 71·0 to 72·0 per cent. carbon, 7·2 to 7·0 hydrogen, and 4·7 nitrogen, agreeing nearly with the above formula (calc. 72·2 carbon, 7·0 hydrogen, 4·7 nitrogen, and 16·1 oxygen), which is the same as that of codeine. According to Bödeker, hydrated pelosine contains 8·21 per cent. water.

Pelosine undergoes alteration in contact with the air, especially under the influence of heat and moisture. It is resinised by moderately strong nitric acid.

The *salts of pelosine* are for the most part very soluble and difficult to crystallise. The solutions give precipitates with auric and platinic chlorides. The *hydrochlorate*, $C^{18}H^{21}NO^3.HCl.H^2O$, is best prepared by passing dry hydrochloric acid gas into a solution of pelosine (previously dried at 120°) in absolute ether. The salt is then deposited in white flocks, which must be washed with the same liquid. When dried it forms an amorphous, very hygrometric powder, very soluble in water and in alcohol. The solution leaves a varnish when evaporated. The salt dried at 110° is anhydrous. The *chloroplatinate* $2(C^{18}H^{21}NO^3.HCl).Pt^{iv}Cl^4$ (at 110°) is a pale yellow, amorphous, strongly electric precipitate. The *chromate*, $C^{18}H^{21}NO^3.Cr^{vi}H^2O^4.H^2O$ (?) is a yellow flocculent precipitate which turns brown during washing, and when heated a few degrees above 100°, decomposes suddenly, giving off chinoline (?) and phenylic alcohol.

**PENCATITE.** A variety of hydrodolomite, found on Vesuvius, and at Predazzo in South Tyrol. Specific gravity 2·534 to 2·613. Contains 26·7 to 29·8 per cent. carbonic anhydride, 35·85 to 35·7 lime, 24·9 to 23·8 magnesia, and 16·6 to 10·7 water, agreeing approximately with the formula $Ca''CO^3.Mg''H^2O^2$. (Roth, J. pr. Chem. xxxvi. 304. Damour, Bull. geolog. [2] iv. 1052.)

**PENGHAWAR DJAMBI.** The hairy stem of an East Indian fern, *Cibotium Cumingii* (i. 962), used for arresting hæmorrhage.

**PENNINE.** A variety of chlorite from Zermatt in the Valais (i. 918).

**PENNITE.** Syn. with HYDRONICKELMAGNESITE (iii. 212).

**PENTA.** A prefix denoting that a compound contains 5 atoms of the element specified: e.g. *pentachloride of phosphorus*, $PCl^5$; *pentachloracetone*, $C^3HCl^5O$.

**PENTACHLOROXYLIN** or **PENTACHLOROXYLONE.** One of the products obtained, according to Gorup-Besanez, by the action of hypochlorous acid on creosote (ii. 105).

**PENTASULPHOPYROPHOSPHATE OF ETHYL.** See SULPHOPHOSPHORIC ETHERS.

**PENTETHYLENIC ALCOHOL.** See ETHYLENE, HYDRATES OF (ii. 577).

**PENTATHIONIC ACID.** See SULPHUR, OXYGEN-ACIDS OF.

**PEPLOLITE.** A mineral from Ramsberg in Sweden, having the composition of a hydrous dichroite (ii. 320). Specific gravity 2·68 to 2·75. Contains 45·95 per cent. silica, 30·51 alumina, 6·77 ferrous oxide, 7·99 magnesia, 0·50 lime, and 8·30 water. (Carlsson, Kongl. Vet. Acad. Förh. 1857, p. 241.)

**PEPSIN.** (Schwann, Müller's Arch. 1836.—Wasmann, Dissert. 1839. Lehm. Phys. Ch. ii. 40.—Brücke, Wien. Acad. Ber. xliii. 601.—Schmidt, Ann. Ch. Pharm. lxi. 22.)—The "active principle" or digestive "ferment" of gastric juice. The name was first used by Schwann. He precipitated gastric juice or acid infusion of stomach with mercuric chloride, suspended the precipitate in water, and got rid of the mercury by sulphuretted hydrogen. The liquid thus obtained very speedily dissolved or digested albumen, &c., at a blood-heat; and Wasmann showed that from it could be precipitated by alcohol a substance which, when redissolved in dilute acids, exhibited the same digestive powers, and to which the name of pepsin was given. Pepsin, thus prepared, was from its reactions judged to be a protein-body. But Mulder obtained artificial digestive fluids, free from proteic reactions, and quite recently Brücke has been able to prepare pepsin in a state of greater purity. An infusion of the glandular layer of the stomach, made with dilute tribasic phosphoric acid, is filtered and neu-

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tralised with lime-water. The bulky precipitate of calcic phosphate, which carries down with it mechanically the greater part of the pepsin, is collected, washed, pressed, and treated with dilute hydrochloric acid. The solution is again precipitated by lime-water, and the deposit again dissolved in dilute acid. To this second solution is gradually added, by means of a long filter reaching down to the bottom of the vessel, a saturated solution of cholesterin in a mixture of 1 part ether and 4 alcohol, and the whole is well shaken. The cholesterin, with the mechanically entangled pepsin, is separated by filtration, well washed, and treated with ether. The ether, holding the cholesterin in solution, is then poured off, and the remaining liquid filtered. The filtrate which, when feebly acidified, acts very energetically on protein-bodies, gives no precipitate with mineral acids, tannin, or mercuric chloride, and only a turbidity with the acetates of lead. It gives no xanthoproteic reaction, and is not coloured by sulphuric acid and sugar, or by strong hydrochloric acid. Pepsin appears, therefore, not to be a protein body; that of previous writers evidently contained other substances beside the actual "ferment" itself.

Pepsin is only active in a dilute acid solution. It is apparently more active in conjunction with hydrochloric than with lactic or other acids. A too high or too low degree of acidity is injurious, 0·08—0·2 per cent. of hydrochloric acid being about the most suitable. Neutralisation suspends, without destroying, the action of a dilute acid solution. Strong alkalis seem, however, to injure pepsin.

The temperature best suited for the action of pepsin is that of the body. According to Brinton, the particular degree varies with the individual temperature of the animal, the pepsin of fishes being inert at the temperature of the mammalian body. In general, temperatures above that of the body are injurious; those below retard the action. A solution of pepsin is completely deprived of its energy by boiling.

Pepsin appears not to be used up or consumed during digestion; that which is poured into the alimentary canal during digestion passes out in part by the urine after it has done its work, and may be recovered from that fluid. Brücke found it also in flesh.

The *modus operandi* of pepsin is unknown. It is usually called a "ferment," but some other name seems to be needed to distinguish its action from such a process as vinous fermentation. The theory that "the action of gastric juice is a transfer to albumen, &c., of a molecular change going on in the gastric juice, pepsin and peptone being essentially analogous to each other in properties," is distinctly negatived by the fact of pepsin not being a protein-compound; and we may infer, from pepsin not being used up in digestion, and from its possessing in itself no great proneness to change, that any "energy" which is concerned in peptonification does not come from the pepsin itself.

Pepsin, as secreted in the so-called peptic glands of the stomach, is neutral; the secretion becomes acid in the ducts of the glands (Brücke). Schmidt supposes that pepsin and hydrochloric acid unite to form a compound acid, the chloro-hydropepsic acid.

The action of pepsin is hindered by the presence of peptones. Hence, when portions of albumen, &c., are successively added to a given quantity of solution of pepsin, the process of digestion is at last arrested. The addition of fresh dilute acid will, however, renew it.

A preparation has become an article of pharmacy under the name of pepsin. It is obtained by drying the glandular layer of pig's or calf's stomach at low temperatures.

M. F.

**PEPTONES.** (Lehmann, Lehrb. i. 318.—Brücke, Wien. Acad. Ber. xxxvii. 131.—Meissner, Zeitschr. Rat. Med. vii. 1, viii. 280, x. 1, xii. 46, xiv. 78, 303.) —Derivatives of the protein-bodies arising during the process of digestion; albuminose of Mialhe. According to Lehmann and Mulder, the peptones are white amorphous bodies, insoluble in alcohol but readily soluble in water, the solution reddening litmus. They form soluble neutral compounds with alkaline and earthy bases. The feebly acid solutions are not coagulated by boiling, not precipitated by alcohol, mineral acids, carbonate of ammonium, sulphate of sodium, neutral acetate of lead, or ferrocyanide of potassium, but by tannin and mercuric chloride. They turn the plane of polarisation to the left, and give Millon's and the xanthoproteic reaction.

Meissner's account of these bodies is as follows. When the opalescent fluid resulting from the digestion of coagulated albumen with pepsin and hydrochloric acid of 0·1—0·2 per cent. strength, is filtered and carefully neutralised, a white flaky precipitate is thrown down, which may be separated by filtration, leaving the rest of the liquid perfectly clear. The acid solutions resulting from the digestion of casein, muscle-fibre, and blood-fibrin, give, when neutralised, a similar precipitate, which Meissner calls parapeptone. When the clear neutral fluid remaining after the separation of the parapeptone is carefully acidified, so that the amount of free acid is very small, a second precipitate is formed, which also may be removed by filtration, and to which the name of metapeptone has been given (only a very small quantity of this body can be obtained by the digestion of albumen). The filtrate contains the peptones. When fibrin or casein is exposed to artificial digestion, the whole is not dissolved, however long the process may be carried on; a flaky precipitate is always formed, and this Meissner calls dyspeptone. Besides these bodies the solutions always contain various saline, fatty, and extractive bodies, in spite of the most careful clearing of the original protein-substances. Meissner describes the peptone of albumen as giving Lehmann's reactions, but states that the peptone of muscle-fibre is also precipitated by alcohol, the nitrates of mercury and silver, ferrocyanide of potassium, and basic acetate of lead. He further believes that the peptone of fibrin is a mixture of three bodies;—*a.* peptone precipitated by concentrated nitric acid and by ferrocyanide of potassium in the presence of a small quantity of acetic acid; *b.* peptone precipitated by ferrocyanide of potassium only in the presence of much acetic acid, and not at all by nitric acid; *c.* peptone precipitated by neither.

Parapeptone (from albumen) is insoluble in water, but very soluble in dilute acids and alkalis, from its solutions in which it may be precipitated by a mixture of alcohol and ether (but not by alcohol alone), also by tannic acid, basic acetate of lead, and mercuric chloride. From its acid solutions, it is precipitated by concentrated solutions of the neutral alkaline salts, and from its acetic acid solution by ferrocyanide of potassium. It gives Millon's reaction. The parapeptones of fibrin and muscle-fibre are similar to that of albumen. That of casein is distinguished by the precipitate formed by neutral alkaline salts, being soluble in excess of the reagent. Inasmuch as parapeptone appears at every stage of the (artificial) digestion of protein-bodies, increasing in amount as the process continues; and since it cannot by the action of pepsin be converted into peptone, Meissner regards it as a distinct final product, and not as a mere stage. He believes that pancreatic juice has the power, which gastric juice has not, of converting it into peptone. The bodies he has called meta- and dyspeptone he considers as mere temporary modifications of peptone and parapeptone.

Brücke, on the other hand, asserts that parapeptone is easily converted into peptone, is not in any sense a final product, and considers its precipitation from the original opalescent fluid by a neutral salt or by neutralisation, to be a mechanical rather than a chemical process. Others hold parapeptone to be identical with syntonin.

The peptones cannot be produced by the action of dilute mineral acids, in the absence of pepsin, at the temperature of the body, but the change may be brought about by prolonged boiling either with dilute acids or with distilled water. The action of ozone also gives rise to similar products (Gornp-Besanez). Thiry gives the elementary composition of parapeptone as C 51·34, H 7·25, N 16·18, S 2·12, O(+P) 23·11; of peptone (obtained by prolonged boiling with distilled water) C 50·87, H 7·03, N 16·34, S 1·64, O(+P) 24·12, that of the albumen used for the experiments and prepared by neutralising a solution of white of egg in dilute hydrochloric acid of 0·2 per cent. strength, being C 51·37, H 7·13, N 16·00, S 2·12, O(+P) 23·38.

The protein-bodies from the vegetable kingdom are in a similar way changed by the action of pepsin into peptones (and parapeptone). Gelatin appears to be merely dissolved by the acid of gastric juice, not converted into peptones; chondrin is split up into a peculiar sugar (cartilage-sugar) and a nitrogenous body resembling gelatin. (Meissner.) M. F.

**PER.** A prefix used, for the most part, to denote that the compound to which it belongs is the highest of a certain series: *e.g.* perchloride of phosphorus $PCl^5$, peroxide of manganese $MnO^2$. The term *peroxide* was formerly restricted to oxides like $MnO^2$ and $PbO^2$, which give up a certain portion of their oxygen when treated with acids, and form salts corresponding to lower oxides; but this use of the word is now nearly obsolete.

**PERBROMIC ACID.** $BrHO^4$. (Kämmerer, J. pr. Chem. xc. 190; Bull. Soc. Chim. 1863, i. 129.)—Obtained by the action of bromine on perchloric acid. On evaporating the liquid over the water-bath, perbromic acid remains as a colourless oil, which is not decomposed by hydrochloric, sulphurous or sulphydric acid. *Perbromate of potassium* is obtained as a crystalline precipitate on mixing concentrated solutions of perbromic acid and caustic potash or chloride of potassium: it is more soluble than perchlorate of potassium, but less soluble than the bromate.—The *barium-salt* is very soluble in boiling water.—The *silver-salt* is sparingly soluble in cold, much more soluble in boiling water, and crystallises in long needles on cooling.

**PERCHLORATES.** $MClO^4$ or $M''Cl^2O^8$, according to the atomicity of the metal. The general characters of these salts have been already described (see CHLORINE, OXYGEN-ACIDS OF, i. 910).

***Perchlorate of Ammonium***, $NH^4ClO^4$, forms transparent rectangular prisms with dihedral summits; isomorphous with the potassium-salt (p. 375); $a : b : c = 0·7926 : 1 : 0·6409$. Angle $\infty P : \infty P$ (macr.) $= 76° 41'$; $P\infty : P\infty$ (basal) $= 77° 55'$ (**Kopp**). It is soluble in 5 pts. water, somewhat soluble also in alcohol. The solution when evaporated gives off ammonia and bromic acid. It is soluble in excess of perchloric acid, and is therefore precipitated by the latter.

***Perchlorate of Barium***, $Ba''Cl^2O^8$, obtained by saturating the acid with caustic baryta or barytic carbonate, or by decomposing the zinc-salt with baryta-water, crystallises in long deliquescent prisms, easily soluble in water and in alcohol. Paper saturated with the aqueous solution burns with a green flame. (**Serullas.**)

***Perchlorate of Cadmium.*** $Cd''Cl^2O^8$. Deliquescent, but crystallises when its aqueous solution is evaporated by heat. (**Serullas.**)

***Perchlorate of Calcium.*** $Ca''Cl^2O^8$. Very deliquescent, crystallises in prisms soluble in alcohol. (**Serullas.**)

***Perchlorate of Copper***, $Cu''Cl^2O^8$, form large blue deliquescent crystals.

***Basic Perchlorate of Cuprammonium.*** $(N^2H^6Cu'')''Cl^2O^8.2(NH^4)HO = \left.\begin{matrix}H^{16}\\ Cu''\\ (ClO^3)^2\end{matrix}\right\}\begin{matrix}N^4\\ O^4\end{matrix}$, obtained by dissolving cupric carbonate in perchloric acid, supersaturating with ammonia, and covering the solution with a layer of alcohol, *forms* dark blue non-deliquescent crystals which crumble to a green powder on exposure to the air. The concentrated aqueous solution is completely decomposed by boiling into free ammonia, perchlorate of ammonium, and black oxide of copper. (**Roscoe**, Ann. Ch. Pharm. cxxi. 346.)

***Perchlorates of Iron.***—The *ferrous salt*, $Fe''Cl^2O^8$, obtained by precipitating ferrous sulphate with perchlorate of barium, forms long colourless needles which may be exposed to the air for some time without decomposing, but ultimately turn yellow from formation of basic salt (**Serullas**). By dissolving metallic iron in dilute hydrochloric acid, the salt is obtained in small, greenish-white, very deliquescent crystals, containing $Fe''Cl^2O^8.6H^2O$, which do not give off their water either in vacuo over oil of vitriol or at 100°, but decompose at higher temperatures (**Roscoe**). The *ferric salt* is not known.

***Perchlorates of Lead.***—A solution of lead-oxide in aqueous perchloric acid yields by spontaneous evaporation, a mass of indistinct spicular crystals of the neutral salt ($Pb''Cl^2O^8.3H^2O$, according to **Roscoe**), easily soluble in water, and having a sweetish astringent taste. The crystals do not give off their water in vacuo or at 100° (**Roscoe**). On boiling the concentrated solution with a large excess of lead-carbonate, and evaporating, indistinct lustreless crystals are obtained, which are resolved by water into a soluble and an insoluble portion; and the solution thus obtained yields on evaporation a *basic salt*, $Pb''Cl^2O^8.Pb''H^2O^2$, in crystals of two different forms, one of which becomes dull when taken out of the liquid, while the other remains bright and transparent. (**Marignac**, *Recherches sur les formes crystallines*, &c., Genève, 1835, p. 36.)

***Perchlorate of Manganese.*** $Mn''Cl^2O^8$.—Deliquescent, soluble in alcohol, not crystallisable.

***Perchlorates of Mercury.***—The *mercurous salt*, $Hg'ClO^4.3H^2O$ (**Roscoe**), crystallises in small concentric needles which do not alter on exposure to the air at ordinary temperatures (**Serullas**), and do not give off their water in vacuo or at 100° (**Roscoe**). The *mercuric salt*, $Hg''Cl^2O^8$, crystallises when evaporated by heat, in colourless, rectangular, very deliquescent prisms, which dissolve in alcohol, leaving a white substance which turns red during filtration, and consists mainly of mercuric oxide. The liquid filtered from this precipitate yields on evaporation a mixture of mercurous and mercuric oxide. (**Serullas.**)

***Perchlorate of Potassium.*** $KClO^4$.—This salt is produced by the decomposition of the chlorate: 1. Chlorate of potassium is kept in a state of fusion till it begins to assume a pasty condition, or till about four litres of oxygen gas have been given off for every thirty grammes of the salt. The residue then consists of a mixture of perchlorate and chloride of potassium:

$$2KClO^3 \quad = \quad KClO^4 \quad + \quad KCl \quad + \quad O^2.$$

If it still contains undecomposed chlorate, a sample treated with hydrochloric acid will exhibit a yellow colour; in this case the heating must be prolonged. On dissolving the residual saline mass in the smallest possible quantity of boiling water, and leaving the solution to cool, perchlorate of potassium separates in small shining crystals which may be freed from chloride by recrystallisation.

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2. Chlorate of potassium is fused at a gentle heat, then introduced in as large pieces as possible into a retort, and covered with three and a-half to four times its weight of strong sulphuric acid. The previous fusion of the salt is necessary, to diminish the number of points of contact with the acid, and thus to moderate the action, which might otherwise become so rapid as to cause a dangerous explosion. As soon as the mass has ceased to give off a yellow gas, the retort must be plunged into water heated not above 60°, and to such a depth as to warm only the saline mixture, not the gas above it. The saline mass becomes colourless after a while, and then consists of a mixture of acid sulphate and perchlorate of potassium, the latter of which may be crystallised from boiling water and purified by recrystallisation as before.

3. Perchlorate of potassium may also be obtained by heating the chlorate with strong nitric acid (Penny, J. pr. Chem. xxiii. 296).—4. By electrolysis of the chlorate (Stadion).

Perchlorate of potassium crystallises in limpid right rhombic prisms, $\infty P\ .\ \bar{P}\infty$, the latter often predominant; also with oP and other faces. Ratio of axes $a : b : c$ = 0·7817 : 1 : 0·6408. Angle $\infty P : \infty P$ in the macrodiagonal principal section = 76° 2′, $\breve{P}\infty : \bar{P}\infty$ (basal) = 78° 41′ (Kopp). The crystals are anhydrous but contain a little decrepitation-water. The salt has a slight taste like that of the chloride, dissolves in 65 pts. water at 15°, in a much smaller quantity of boiling water, and is insoluble or very sparingly soluble in alcohol (Serullas). According to Roscoe, it is as soluble in absolute alcohol as carbonate of barium in water, but in alcohol containing a small quantity of acetate of potassium it is absolutely insoluble. When heated above 400° it is resolved into oxygen and chloride of potassium. It deflagrates slightly on red-hot coals. In consequence of the sparingly solubility of this salt in water, perchloric acid forms a precipitate in the solutions of nearly all potassium-salts, even of alum and tartar-emetic.

*Perchlorate of Silver*, $AgClO^4$, does not crystallise, but forms a white powder which deliquesces in the air and is soluble in alcohol. The aqueous solution turns brown in sunshine. The dry salt may be fused without much decomposition, and solidifies in the crystalline form on cooling; but at a higher temperature it suddenly gives off oxygen, and leaves chloride of silver. (Serullas.)

*Perchlorate of Sodium*, $NaClO^4$, may be prepared by direct combination, or by heating the chlorate with strong nitric acid. It is deliquescent, soluble in alcohol, and separates from the solution in transparent laminæ (Serullas); rhombohedrons (Penny).

*Perchlorate of Zinc*, $Zn''Cl^2O^8$, crystallises by evaporation in tufts of deliquescent needles, soluble in alcohol.

**PERCHLORIC ETHER.** $C^2H^5ClO^4$. *Ethylic Perchlorate. Perchlorate of Ethyl.* (Clark, Hare and Boyle, Phil. Mag. [3] xix. 370.—Roscoe, Chem. Soc. J. xv. 213.)—This compound is best prepared by distilling a mixture of ethyl-sulphate and perchlorate of barium. An alcoholic solution of perchlorate of silver treated with ethylic iodide, even at −10°, yields merely perchloric acid and ethylic oxide, and on bringing perchloric acid in contact with alcohol or ether, a violent explosion generally takes place. 1 at. perchlorate of barium is rubbed to a fine powder with 1 at. crystallised ethyl-sulphate of barium; and a small quantity of the mixture, not exceeding 80 grains (on account of the danger of explosion), is introduced into a small retort connected with a tube-shaped receiver surrounded with ice and heated in an oil-bath provided with a thermometer, by means of an Argand lamp, which can be quickly removed. A wooden screen with holes filled up with plates of glass must be placed for protection between the operator and the retort. No action takes place till the temperature rises to 100°, and so long as the water (of crystallisation) has not passed over, there is no fear of explosion. But above 100°, the heat must be very slowly raised to 171°, at which temperature the distillation comes to an end:

$$C^4H^{10}Ba''S^2O^8 + Ba''Cl^2O^8 = 2Ba''SO^4 + 2C^2H^5ClO^4.$$

With perchlorate of potassium the operation does not succeed; neither can the ether be obtained by the use of ethyl-sulphuric acid instead of the barium-salt.

The perchloric ether collects in the receiver, covered with a layer of water. The water is removed, without taking the receiver in the hand, which might cause an explosion—by means of a strip of paper moistened at the end. To preserve the perchloric ether without danger, it may be mixed with absolute alcohol; for a mixture of 1 to 2 parts absolute alcohol with the perchloric ether obtained from 1 pt. ethyl-sulphate of barium does not explode. The pure ether may be again separated from this mixture by the addition of an equal bulk of water; the separation is however always attended with loss, because the water exerts a decomposing action on the ether. All manipulations with this compound should be performed with gloves on the hand, and a mask with thick eye-glasses before the face. (Hare and Boyle.)

Roscoe distils an intimate mixture of equal weights (10 grms.) of the two salts in a small retort heated in an oil-bath, the neck of the retort being bent downwards, and passing into a test-tube containing a small quantity of water. About 2 cub. cent. of an oily liquid heavier than water then passes over between 140° and 160°, and at 170° white fumes of perchloric acid are given off. The oily distillate is purified by repeated washing with water.

Perchloric ether is a transparent and colourless liquid, heavier than water, of agreeable odour, and sweet, afterwards bitter, cinnamon-like taste, insoluble in water, soluble in ether. At 100° it either explodes or swells up. It is the most violently explosive of all known compounds, the explosion being induced by heat, friction, percussion, and often taking place without any external cause. When dry it explodes on being merely poured from one vessel to another. The least drop exploded on an open porcelain basin crumbles it to powder. If the above-mentioned mixture of perchloric ether with alcohol be poured into a basin containing an equal quantity of water, the greater part of the hydrated alcohol poured off from the drop of perchloric ether which falls to the bottom, and the remaining liquid thrown on a wet filter supported by a wire funnel, so that the watery liquid may run off, the drop of perchloric ether which remains on the filter may be exploded by contact with a hot body or by the blow of a hammer. Its solution in a sufficient quantity of alcohol, however, burns away completely, when set on fire, without the least explosion. (Hare and Boyle.)

Perchloric ether does not decompose when kept under water; but undergoes partial decomposition when separated by water from its alcoholic solution.—Alcoholic potash added to the mixture of perchloric ether and alcohol instantly produces complete decomposition of the ether, and throws down a larger quantity of potassic perchlorate.

**PERCHLOROPLATINOCYANIDES.** See PLATINUM, CYANIDES OF (ii. 268).

**PERCHLOROQUINONE.** See QUINONE.

**PERCHLORORUBIAN.** See RUBIAN.

**PERCHLOROXYNAPHTHALIC ACID.** See OXYNAPHTHALIC ACID (p. 313).

**PERCYLITE.** A mineral, crystallised in cubes, from Sonora in Mexico, containing, according to Percy, chlorine, lead and copper, in the proportion 0·84 : 2·16 : 0·77, whence he regards it as $\overset{\prime\prime}{\mathrm{Pb}}{}^2\mathrm{Cl}^2\mathrm{O}.\overset{\prime\prime}{\mathrm{Cu}}{}^2\mathrm{Cl}^2\mathrm{O}.\mathrm{H}^2\mathrm{O}$. (Phil. Mag. [3] xxxvi. 131; Jahresb. 1850, p. 763.)

**PEREIRINE.** An alkaloïd occurring in the bark of Pao Pereira (*Vallesia inedita*), an apocyanaceous tree growing in the Brazilian forests: it possesses febrifugal properties. (Goos, Pharm. Centr. 1839, p. 610.—Peretti, Annali medic. chirurg. di Roma, i. fascic. 3.)

**PERICLASE.** Magnesia with 6 to 8·5 per cent. ferrous oxide, occurring in cubes on Monte Somma, disseminated through ejected masses of a white lime-stone, and in spots of clustered crystals, sometimes with white olivine and earthy magnesite. (Damour, Ann. Min. [3] iv. 381.—Scacchi, J. pr. Chem. xxviii. 486.)

**PERICLIN.** Syn. with ALBITE (see FELSPAR, ii. 621).

**PERIDOTE.** Syn. with OLIVIN (p. 201).

**PERIMORPHOUS CRYSTALS.** Crystals consisting of an envelope of one mineral with a nucleus of another, the external form of the crystal being that of the envelope; for example at Arendal crystals are found having the form of garnets and an external envelope of that mineral, while the interior consists of calcspar (Jahresb. 1858, p. 740; 1861, p. 965).

**PERIODIC ACID.** See IODINE, OXYGEN-ACIDS OF (iii. 307).

**PERISTERITE.** Albite from Perth, Lower Canada (see FELSPAR, ii. 622).

**PERLITE.** Syn. with PEARLSTONE (p. 358).

**PERMANENT WHITE.** Sulphate of barium, used as a water-colour pigment.

**PERMANGANATES.** See MANGANIC ACIDS (iii. 819).

**PEROFSKITE** or **PEROWSKITE.** Titanate of calcium, occurring in cubes and other monometric forms at Achmatousk near Slatoust in the Ural (see TITANATES).

**PEROWSKIN.** See TRIPHYLIN.

**PEROXIDES.** See OXYGEN (pp. 304, 309).

**PERSPIRATION.** (Favre, Compt. rend. xxxv. 721.—Schottin, Arch. Phys. Hlk. xi. 73.—Funke, Molesch. Untersuch. iv. 36.—Lehmann, Lehrb. ii. 326.)—Material passing away from the body by way of the skin. According to Seguin, the body loses by skin and lungs 18 grains per minute, of which 11 grains pass off by the skin and 7 grains by the lungs. A large portion leaves the body in a state of gas or vapour, constituting what is called the "insensible" perspiration. This consists mainly of watery vapour, the amount of which varies within wide limits according to the temperature and moisture of the atmosphere, the quantity and character of the food and drink taken, the condition of the body, whether at rest or at work, &c. It is in fact this evaporation which regulates the temperature of the body. Besides watery vapour, "insensible" perspiration contains carbonic acid, nitrogen (?) (see Respiration), and small quantities of volatile and odoriferous matters.

That which remains on the surface of the body as a liquid is called the "sensible" perspiration or sweat. It is said to be secreted by the sudoriparous glands of the skin, and also, according to some authors, by the portions of skin between those glands. Over most parts of the body sweat is mixed with a fatty secretion derived from the so-called sebaceous glands.

This sebaceous secretion, which when gathered in masses forms the *vernix caseosa* and *smegma præputii*, consists principally of fatty bodies, palmitin, olein, with their soaps and cholesterin, a protein body resembling casein, extractives, and salts, viz. chloride of sodium, with earthy and alkaline phosphates.

Sweat, when obtained in a tolerably pure state, is a clear colourless fluid with no morphological constituents beyond epidermic scales. When fresh, its reaction is acid, of variable intensity; but according to Favre, during a prolonged and copious sweat, the reaction, at first acid, becomes after a while neutral, and at last alkaline. The odour of sweat, often very marked, varies with the situation whence it has been obtained. The amount of solid constituents varies exceedingly; in general it is in inverse ratio to the rapidity of secretion, up to a certain limit, beyond which it remains constant. Funke gives 1·18 per cent. as an average, ·962 per cent. being the mean for the organic, ·329 per cent. for the inorganic substances. The total amount of sweat varies extremely.

As normal constituents of sweat may be mentioned—1. Various acids: mainly formic, with butyric and acetic, and possibly propionic, caproic and caprylic. The existence of lactic acid (Berzelius) has been denied by later observers.—2. Neutral fats, which, since they have been found in parts, such as the palm of the hand, destitute of sebaceous glands, must be reckoned as true elements of sweat: cholesterin, palmitin, olein, stearin.—3. Nitrogenous bodies: the sudoric or hydrotic acid of Favre, urea (leucine, tyrosine?). Most observers have failed to find the former; the latter has been determined by Funke, who found as much as 0·112 and 0·199 per cent. in a total dry residue of ·696 and ·790 per cent. Other inquirers also have detected urea in sweat (according to Meissner, the amount of it varies with the nature of food taken), and yet Ranke failed to find it (see Nutrition, p. 152).—4. Salts: chiefly chloride of sodium, with chloride of potassium, alkaline and earthy phosphates, alkaline sulphates, and a trace of iron. According to Schottin, there is also a colouring matter. The amount of epithelium is 0·42 per cent., Schottin, or 0·206—0·233, Funke.

The following substances are said to have been observed at various times as abnormal constituents of sweat: Albumen, urea (in large quantities in cholera), uric acid, oxalate of calcium, lactic acid, sugar, bile-pigments, indigo in blue sweat, black colouring matter in black sweat, and blood in "bloody sweat." Benzoic (partly as hippuric), succinic and tartaric acids, iodine and iodide of potassium, have when taken internally been detected in the perspiration. M. F.

**PERSPIROYLIC ACID.** Syn. with Salicylic Acid.

**PERSULPHIDES, AMYL-DISULPHOCARBONIC** and **ETHYL-DISULPHOCARBONIC.** See Sulphocarbonic Ethers.

**PERSULPHOCYANIC ACID.** $C^2H^2N^2S^3 = Cy^2H^2S^3$. *Persulphocyanhydric* or *Hydropersulphocyanic acid, Sulphuretted Hydrosulphocyanic acid, Hydroxanthic acid.* (Wöhler, Gilb. Ann. lxix. 271.—Woskresensky, *Traité de Chimie organique par Liebig*, i. 192.—Liebig, Ann. Ch. Pharm., xliii. 96.—Völckel, Pogg. Ann. lviii. 138; lxi. 149; lxii. 150;—Ann. Ch. Pharm. lxxxix. 127.)—This body was discovered in 1821 by Wöhler, but was confounded for some time with persulphocyanogen; till the distinction between the two was pointed out by Woskresensky and by Völckel.

It is produced by the metamorphosis of sulphocyanic acid, CyHS, under the influence of mineral acids; also, under certain circumstances, by the spontaneous decomposition of sulphocyanates:

$$\underset{\text{Sulphocyanic acid.}}{3CyHS} = \underset{\text{Hydrocyanic acid.}}{CyH} + \underset{\text{Persulphocyanic acid.}}{Cy^2H^2S^3}$$

It is prepared:—1. By mixing a cold saturated aqueous solution of sulphocyanate of potassium with from 6 to 8 times its bulk of strong hydrochloric acid. The mixture at first coagulates into a white gelatinous magma, which turns yellow in a few minutes, gives off carbonic anhydride and hydrocyanic acid, after the lapse of an hour, and is converted into a mass consisting of a liquid and needles of persulphocyanic acid. The needles, if collected after 24 hours and washed with cold water, constitute the pure acid (Völckel). The decomposition takes place just as well with a dilute solution of sulphocyanate of potassium; but the separation of the needles is slower.—Another method is to saturate a solution of sulphocyanate of potassium in 5 parts of water, keeping it cold, with hydrochloric acid gas: the persulphocyanic acid then separates after a while, on cooling, in the form of a yellow powder. If, however, the liquid be suffered to get warm from the absorption of the hydrochloric acid, part of the separated sulphocyanic acid volatilises undecomposed; the mixture likewise gives off carbonic anhydride after a while, sometimes also sulphuretted hydrogen and sulphide of carbon; and there are formed in it, hydrocyanic acid, formic acid, and ammonia, by which products the yield of persulphocyanic acid is diminished, the amount of diminution being greater as the solution of sulphocyanide of potassium is more dilute, and its temperature rises higher (Völckel).—2. By passing dry hydrochloric acid gas over melted sulphocyanate of potassium contained in a tubulated retort, whereupon sulphide of carbon and hydrocyanic acid are evolved, and persulphocyanic acid sublimes. The latter is purified by dissolving it in boiling alcohol, from which it separates out again on cooling. (Liebig.)

Persulphocyanic acid thus obtained is a pale yellow crystalline powder, tasteless and inodorous, nearly insoluble in cold *water*, sparingly soluble in boiling water, whence it separates in splendid yellow needles on cooling; soluble also in *alcohol* and in *ether*. The solutions have a slight acid reaction, and form precipitates with the salts of many of the heavy metals.

Persulphocyanic acid decomposes at about 200°, giving off chiefly sulphide of carbon, and finally ammonia and sulphur; if the heat has been rather strong, the residue consists of hydromellone (iii. 874); if it has been lower, the residue reacts like a mixture of sulphur and melam. According to Gerhardt's formula of melam and hydromellone (iii. 866, 874) the decomposition may be represented by the equations:

$$\underset{\text{Persulphocyanic acid.}}{3C^2N^2H^2S^3} = 3CS^2 + S^3 + \underset{\text{Melam.}}{C^3N^6H^6}$$

and

$$\underset{\text{Melam.}}{2C^3N^6H^6} = 3NH^3 + \underset{\text{Hydromellone.}}{C^6N^9H^3}$$

or, according to Liebig's formulæ (*loc. cit.*);

$$\underset{\text{Persulphocyanic acid.}}{6C^2N^2H^2S^3} = 6CS^2 + S^6 + NH^3 + \underset{\text{Melam.}}{C^6N^{11}H^9}$$

and

$$\underset{\text{Melam.}}{C^6N^{11}H^9} = 2NH^3 + \underset{\text{Hydromellone.}}{C^6N^9H^3}$$

Small quantities of sulphydric and sulphocyanic acid are likewise found among the products.

Völckel, by heating persulphocyanic acid to various temperatures, obtained a number of brown or yellow amorphous residues, of varying composition, which he regarded as sulphides of peculiar radicles (*xuthene*, *melene*, *xanthene*, &c.); but they were probably nothing but mixtures.

Persulphocyanic acid is but slightly attacked by *hydrochloric acid* at common temperatures; at the boiling heat, however, it is partly resolved into carbonic anhydride, ammonia, sulphydric acid, and sulphur:

$$C^2N^2H^2S^3 + 4H^2O = 2CO^2 + 2NH^3 + 2H^2S + S.$$

*Nitric acid*, especially when hot, converts it into carbonic anhydride, sulphuric acid, and ammonia. It dissolves, without alteration, in cold strong *sulphuric acid*, and is reprecipitated by water; but on boiling the solution sulphurous anhydride is evolved: —*Chlorine* decomposes persulphocyanic acid, especially with aid of heat, forming chloride of sulphur, chloride of cyanogen, hydrochloric acid, and a brown-red body insoluble in water.—By caustic *alkalis* it is gradually converted into sulphocyanate and free sulphur: $Cy^2H^2S^3 = 2CyHS + S$.

**Persulphocyanates.**—The solutions of persulphocyanic acid in aqueous alkalis may be regarded, when recently prepared, as persulphocyanates, though, as just observed, they are gradually converted into sulphocyanates. These solutions, as well as the aqueous acid, form yellow precipitates with *stannous chloride*, *cupric sulphate*, and *nitrate of lead:* with *nitrate of silver* a yellow precipitate which quickly decomposes, with formation of sulphide of silver; and with *platinic chloride* a brownish-yellow precipitate. The salts of the other heavy metals are not precipitated by soluble persulphocyanates.

*Persulphocyanate of Lead.* $Cy^2Pb''S^3$.—Obtained by precipitating a boiling aqueous solution of the acid with neutral acetate of lead; resembles chromate of lead in external characters, and is perfectly insoluble in water, alcohol, and dilute acids.—With *basic acetate of lead*, a precipitate is formed containing $Cy^2Pb''S^3.Pb''O$.

**PERSULPHOCYANOGEN.** $C^3N^3HS^3 = Cy^3HS^3$? *Pseudosulphocyanogen, Sulphide of Cyanogen, Cyanoxisulfide.* (Wöhler, Gilb. Ann. lxix. 271.—Liebig, Ann. Ch. Pharm. x. 1; xi. 12; xxv. 4; xxxix. 199, 201, 212; l. 337.—Parnell, Rev. scient. v. 149.—Völckel, Ann. Ch. Pharm. xliii. 80; lxxxix. 127; Pogg. Ann. lviii. 145; lxii. 607.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xix. 98.—Jamieson, Ann. Ch. Pharm. lix. 339.—Gm. viii. 108.—Gerh. i. 447.—A compound produced by the action of chlorine or boiling dilute nitric acid on aqueous sulphocyanate of potassium. It is an orange-yellow precipitate, insoluble in *water*, *alcohol*, and *ether*, soluble in strong *sulphuric acid*, whence it is precipitated by water without alteration. It was formerly regarded as *sulphocyanogen* CNS, the radicle of the sulphocyanates; but its constitution is really more complex. The analyses made of it by different chemists also differ considerably, as will be seen by the following table:—

| | Liebig. | Parnell. | Völckel. | | | Jamieson. | Laur. & Gerh. |
|---|---|---|---|---|---|---|---|
| | | | *earlier.* | *later.* | | | |
| Carbon . | | 20·06 | 19·93 | 20·20 | 20·31 | 19·17 | 20·45 |
| Nitrogen . | | 23·23 | 23·31 | | | 22·36 | |
| Sulphur . | 55·84 to 56·15 | 52·59 | 52·68 | 54·26 | | 50·88 | 53·90 |
| Hydrogen . | 0·33 to 0·96 | 0·92 | 1·08 | 0·90 | 0·91 | 1·58 | 0·66 |
| Oxygen | | 3·20 | 3·00 | | | 6·01 | |
| | | 100·00 | 100·00 | | | 100·00 | |

All these analyses were made with persulphocyanogen obtained by the action of chlorine on aqueous sulphocyanate of potassium.—Liebig dried it in vacuo before analysing it.—Parnell dried it partly over the water-bath, partly at 242°, at which latter temperature a slight odour of cyanogen was apparent.—Völckel does not state the temperature at which his substance was dried.—Jamieson boiled the precipitate with water as long as anything was dissolved out, and examined the pure yellow powder which remained. During this boiling, the odour of cyanogen was perceptible, and the water dissolved sulphocyanic acid, together with a small quantity of another sulphur-compound. As the preparation might have been decomposed during this long boiling, and moreover it is not stated how the substance was dried before analysis, the analytical results are not much to be trusted, especially as the amount of oxygen comes out too great. This amount of oxygen is regarded by Liebig (Ann. Ch. Pharm. l. 337) as very problematical, inasmuch as, in the dry distillation of pseudosulphocyanogen, no oxygenised product is obtained, except water.—Laurent and Gerhardt dried the portion of the precipitate which appeared under the microscope to be perfectly free from crystals (probably of persulphocyanic acid) for a long time, and at high temperature. Their analysis, which agrees very nearly with the more recent analyses by Völckel, leads to the formula $C^3N^3HS^3$ (calc. 20·57 C, 24·00 N, 54·86 S, and 0·57 H), according to which persulphocyanogen is formed from persulphocyanic acid by substitution of 1 at. cyanogen for 1 at. hydrogen.

Persulphocyanogen when *heated* gives off sulphide of carbon and free sulphur, leaving a residue of hydromellone:

$$3C^3N^3HS^3 \quad = \quad 3CS^2 \quad + \quad S^3 \quad + \quad C^6N^9H^3.$$

If moisture is present, ammoniacal products are also given off at the commencement of the decomposition. *Chlorine* acts on persulphocyanogen only at high temperatures, forming solid chloride of cyanogen, chloride of sulphur, and a residue of hydromellone.

Persulphocyanogen dissolves easily in a solution of sulphydrate of potassium, yielding sulphocyanate and sulphomellonide of potassium, together with other products:

$$2Cy^3HS^3 + 3KHS + 2H^2O \quad = \quad \underset{\substack{\text{Sulpho-}\\\text{cyanate.}}}{2CyKS} + \underset{\substack{\text{Sulphomel-}\\\text{lonide.}}}{Cy^3H^3KNS^2} + 3H^2S + CO^2 + S^2.$$

Persulphocyanogen dissolves slightly in *ammonia* (Wöhler); abundantly (Liebig). When boiled with *potash*, it forms a solution which gives with ferric salts the reaction of sulphocyanic acid. By triturating persulphocyanogen with strong potash, adding a large quantity of water, then an excess of lead-acetate, and lastly sufficient acetic acid to produce an acid reaction, Völckel obtained a brownish-yellow precipitate, apparently consisting of $2Cy^3Pb''S^4.Pb''H^2O^2$.

*Hydrothiocyanic acid.*—When persulphocyanogen is boiled with potash, and hydrochloric acid added to the solution, a yellow powder is precipitated which dissolves in 42 pts. of boiling water, and the solution forms with acetate of lead a yellow precipitate of *hydrothiocyanate of lead*, $Cy^3HPb''S^3O$. The acid, $Cy^3H^3S^3O$, may be regarded as formed from persulphocyanogen by addition of 1 at. $H^2O$. The analysis of the yellow powder above mentioned does not however agree very well with this formula. (Parnell, Völckel.)

**PERTHITE.** Orthoclase from Perth in Canada. See FELSPAR (ii. 620).

**PERU BALSAM.** See BALSAMS (i. 496).

**PERURIC ACID.** An acid obtained, according to Unger (Pogg. Ann. lxv. 222), by gently heating guanine with a mixture of chlorate of potassium and hydrochloric acid. It crystallises in shortened prisms with rhombic base, or in tufts of colourless crystals destitute of taste and smell. Contains 31·26 per cent. carbon and 2·60 hydrogen; ratio of carbon to nitrogen 10·4; whence it is probably $C^{10}H^8N^8O^8.H^2O$.

**PERUVIN.** Syn. with STYRONE or CINNYLIC ALCOHOL (i. 992).

**PETALITE.** *Castor.*—A silicate of aluminium and lithium, also containing sodium, in which lithia was discovered by Arfvedson in 1818. It occurs massive, with apparently monoclinic structure, exhibiting three cleavages in one zone, affording the angles 117°, 142° and 101°, the cleavages inclined at 142° are the most distinct. Hardness = 6 to 6·5. Specific gravity = 2·42 (Arfvedson); 2·45 (Clarke); 2·426 (C. G. Gmelin). It has a vitreous and glistening lustre, pearly on the faces of perfect cleavage, and a white or grey colour, with occasionally a reddish or greenish tinge. Streak white. Translucent. Fracture imperfect conchoïdal.

When heated before the blowpipe, either alone or with fluor-spar and acid sulphate of potassium, it colours the flame transiently red, behaving in other respects like orthoclase. It is not attacked by acids.

*Analyses.*—1. From Utö: *a.* By Arfvedson (Schw. J. xxii. 93):—*b.* By C. Gmelin (Gilb. Ann. lxii. 399);—*c.* Reddish;—*d.* Whitish, by Waltershausen (*Vulks. Gest.* p. 295):—*e.* By Hagen (Pogg. Ann. xlviii. 361);—*f.* Specific gravity 2·447—2·455, by Rammelsberg (*ibid.* lxxxv. 544).—2. From Bolton, Massachusetts, by Smith and Brush (Sill. Am. J. [2] xvi. 365).—3. From Elba (the variety called *Castor*; by Plattner, Pogg. Ann. lxix. 436, 443):

| | 1. | | | | | | 2. | 3. |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | | |
| Silica . . . | 79·21 | 74·17 | 76·74 | 74·60 | 77·22 | 77·79 | 77·93 | 98·01 |
| Alumina . . | 17·22 | 17·41 | 18·66 | 16·94 | 17·47 | 18·58 | 16·24 | 18·85 |
| Lithia . . . | 5·76 | 5·16 | 2·69 | 2·98 | 2·67 | 3·30 | 3·63 | 2·76 |
| Soda . . . | . . | | . . | 0·05 | 2·29 | 1·19 | 0·50 | |
| Limo . . . | . . | 0·32 | 0·62 | 0·73 | | | | |
| Magnesia . . | . . | . . | 0·10 | 0·10 | . . | . . | 0·24 | |
| Ferric oxide . . | . . | . . | 0·18 | 0·16 | . . | . . | 0·56 | 0·61 |
| Loss by ignition . | . . | 2·17 | 0·97 | 0·92 | . . | . . | 0·65 | |
| | 102·19 | 99·23 | 99·96 | 96·48 | 99·65 | 100·86 | 99·75 | 100·23 |

According to these analyses, petalite may be regarded as $3(M^2O.2SiO^2).4(\overset{\prime\prime\prime}{Al}{}^2O^3.6SiO^2)$ or perhaps as $3(M^2O.3SiO^2).2(2\overset{\prime\prime\prime}{Al}{}^2O^3.9SiO^2)$. Castor may be approximately represented by the formula $(Li^2O.3SiO^2).(2\overset{\prime\prime\prime}{Al}{}^2O^3.9SiO^2)$ or by $(Li^2O.2SiO^2).2(\overset{\prime\prime\prime}{Al}{}^2O^3.6SiO^2)$.

**PETASITE.** A resin obtained from the root of *Tussilago petasites.* It is not altered by caustic soda. Its alcoholic solution mixed with mineral acids assumes an emerald-green colour, changing to blue in the case of hydrochloric acid. (Reinsch, N. Jahrb. Pharm. iv. 257.)

**PETININE.** An alkaloïd, isomeric if not identical with tetrylamine, $C^4H^{11}N$, occurring in the most volatile portion of bone-oil. (See TETRYLAMINE.)

**PETROL.** $C^8H^{18}$. (Bussenius and Eisenstück, Ann. Ch. Pharm. cxiii. 151.) —A hydrocarbon (not isolated) occurring in the petroleum of Sehnde near Hanover. On distilling the crude petroleum with steam at a pressure of 4 or 5 atmospheres, and rectifying the naphtha which passes over, a portion is obtained boiling below 180° and consisting of petrol together with olefines and homologues of marsh-gas. The petrol cannot be separated by fractional distillation, but by treatment with a mixture of strong nitric and sulphuric acids, it may be converted into a crystalline compound, viz.:

*Trinitropetrol*, $C^8H^7(NO^2)^3$.—To prepare this compound, 2 pts. oil of vitriol, 1 pt. nitric acid of specific gravity 1·5, and 2 pts. of the above-mentioned distillate, boiling below 180°, are disposed one over the other in layers in a tubulated retort, and left to rest for 24 hours. The action, which would be violent if the liquids were rapidly mixed, then takes place quietly, and trinitropetrol separates between the acid and the oil, as a crystalline mass, which, after the acid and oil[*] have drained off, is purified by washing with water and with lukewarm alcohol, and repeated fractional crystallisation from hot alcohol, the portion which separates below 40° being each time collected apart.

Trinitropetrol crystallises in needles and scales, the latter being formed most abundantly at comparatively low temperatures. It melts at 162°, solidifying again at 135°—140°. It is insoluble in *water*, soluble in *ether*, *benzene*, and cold *alcohol*, more easily (to the amount of $\frac{1}{18}$) in boiling alcohol. It is decomposed by a mixture of *iron filings* and *acetic acid*, but without formation of crystallisable products. With alcoholic *sulphide of ammonium*, it forms two compounds, one of which possesses distinct basic properties, viz.:

*Nitropetroldiamine*, $C^8H^{11}N^3O^2 = \left.\begin{matrix}[C^8H^7(NO^2)]''\\ H^4\end{matrix}\right\}N^2$.—When trinitropetrol is mixed in a retort with alcoholic sulphide of ammonium and sulphydric acid gas is passed into the mixture, a large quantity of sulphur suddenly separates, and nitro-petroldiamine crystallises out. The excess of sulphide of ammonium and the alcohol are removed as completely as possible by distillation, and the nitropetroldiamine is purified by exhausting the residue with boiling alcohol, dissolving the crystals which separate therefrom in dilute sulphuric acid,[†] precipitating the filtered solution with ammonia, repeating this solution and precipitation, and recrystallising the product from alcohol.

Nitropetroldiamine crystallises in long orange-red monoclinic prisms, insoluble in water, sparingly soluble in cold, rather easily in boiling alcohol. It begins to sublime at 210°, melts at 215° (the fused mass solidifying in the crystalline form at the same temperature), and decomposes at a higher temperature, with separation of charcoal. Treated with *nitrous acid*, it yields nothing but brown resinous products.

*Hydrochlorates of Nitropetroldiamine.*—The salt, $C^8H^{11}N^3O^2.HCl$, is obtained in crystals by heating the base with water and a quantity of hydrochloric acid not sufficient for complete solution, and leaving the filtrate to evaporate. A solution of the base in excess of hydrochloric acid yields the salt $C^8H^{11}N^3O^2.2HCl$.

The *chloroplatinate*, $C^8H^{11}N^3O^2.2HCl.Pt^{iv}Cl4.3H^2O$, separates on adding platinic chloride to the solution of the last-mentioned salt, in golden-yellow six-sided microscopic tablets, which dissolve easily in hydrochloric acid, are decomposed by water, with separation of the base, give off their crystallisation-water below 100°, and hydrochloric acid at a temperature a little above that point.

*Sulphates.*—α. On boiling nitropetroldiamine with water, adding dilute sulphuric acid till it is completely dissolved, and leaving the solution to cool, the salt $C^8H^{11}N^3O^2.S^2H^2O^4$ separates in rather large six-sided monoclinic prisms, which are decomposed by water.—β. The mother-liquor of this salt yields by slow evaporation over oil of vitriol, large transparent plates of the salt $C^8H^{11}N^3O^2.2SH^2.O^42H^2O$, which gives off its water at 100°, and like the preceding, is decomposed by recrystallisation from hot water, yielding basic compounds.—γ. On boiling nitropetroldiamine with a quantity of dilute sulphuric acid not sufficient to dissolve the whole, and filtering the solution while hot, the filtrate solidifies to a mass of small yellowish laminæ of the salt $2C^8H^{11}N^3O^2.SH^2O^4.2H^2O$, which gives off its crystallisation-water at 110°.

*Triethylnitropetroldiamine*, $C^{14}H^{23}N^3O^2 = \left.\begin{matrix}[C^8H^7(NO^2)]''\\ H.(C^2H^5)^3\end{matrix}\right\}N^2$.—The hydriodate of this base, $C^{14}H^{23}N^3O^2.HI$, obtained by heating nitropetroldiamine for some time with ethylic iodide in a bath of boiling solution of nitrate of sodium, and purified by recrystallising the solid part of the product from hot water, crystallises in red rhombic prisms with pyramidal faces. On adding ammonia to the solution of this hydriodate in hydrochloric acid, triethyl-nitropetroldiamine is precipitated in lemon-yellow scales; it is soluble in alcohol and in ether, and separates from these solutions on evaporation in oily drops which solidify in the crystalline form after some time only. The solution of the base in hydrochloric acid yields, on addition of platinic chloride, the *platinum-salt* $2(C^{14}H^{23}N^{3}O^{2}.HCl)Pt^{iv}Cl^{4}$, in tufts of slender golden-yellow needles.

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[*] This oily liquid, after washing with water, drying over chloride of calcium, left on rectification a thickish yellow residue which deposited nacreous crystalline laminæ. These crystals exhibited on one occasion a melting point between 155° and 156°, and a composition corresponding with the formula $C^9H^9(NO^2)^3$, whence they appear to consist of the next homologue of trinitropetrol; they also reacted like the latter with sulphide of ammonium.

[†] There then remains undissolved an orange-yellow crystalline compound $C^{16}H^{20}N^6O^9$, insoluble in water, alkalis and dilute acids, soluble in concentrated acids, and separable therefrom by water; sparingly soluble in alcohol, ether, chloroform and sulphide of carbon; melting at 191°—192°, and subliming in small quantity. When subjected to the action of dry hydrochloric acid gas, it forms the somewhat unstable compound $C^{16}H^{20}N^6O^9.2HCl$.

**PETROLENE.** The name applied by Boussingault to the more volatile constituent of asphalt or bitumen (i. 426). See also Völckel (Ann. Ch. Pharm. lxxxvii. 139; Jahresb. 1853, p. 524).

**PETROLEUM.** *Earth Oil, Naphtha, Maltha, Mineral Tar or Oil; Erdöl, Steinol; Bitume liquide.*—A variety of liquids known by some one or other of the above names, and corresponding with vegetal and animal oils in the characters of inflammability and insolubility in water, occur in many parts of the earth. They all agree in possessing a strong bituminous smell, but differ considerably in other physical characters, being sometimes thin, transparent and pale coloured; sometimes viscid, opaque and black. There are also numerous varieties with characters intermediate between these extremes. The specific gravity varies from 0·7 to 1·1, and the colour is frequently brown or greenish. The name *naphtha* has generally been applied to the thinner and least coloured varieties of mineral oil, or to the more volatile portion of the distillate obtained by rectifying the native oil, while the darker and more viscid kinds have been termed *mineral tar*, and the intermediate varieties *petroleum*.

The countries most famous for the occurrence of mineral oil are Persia, the Caucasus and Georgia, Burmah, the West Indian Islands, and North America. It also occurs in the country to the north of the Danube, in Italy, Bavaria, Hanover, Zante, Switzerland, China, India, and to some extent in England and France.

Chemically the substances known by names of naphtha, petroleum, &c., are all very closely allied, inasmuch as they consist for the most part of oils differing in density and volatility. The older analyses of these mineral oils were made without any further attempt at separating the substances they evidently contained in a state of mixture, than merely rectifying the oil and treating it with sulphuric acid. They sufficed, however, to establish the fact that the constituents of petroleum were essentially compounds of carbon and hydrogen; but the chemistry of the hydrocarbons was so slowly developed, after the time when Faraday demonstrated the existence of numerous compounds of this kind, and petroleum was so little used, that scarcely any progress was made towards a knowledge of its constitution until quite recently, since the extensive application of this material to useful purposes has caused greater attention to be directed to it.

A thick black variety of petroleum, occurring between Pcklenicza and Moslowina in Hungary, was examined in 1788 by Winterl, who found that it yielded by distillation a colourless oil, a yellow oil, and a buttery mass. (Crell's Chem. Annal. i. 493.)

A dark brown Galician pretoleum of specific gravity 0·943, was examined in 1791 by Martinovich, who obtained from it by distillation a yellow oil of specific gravity 0·811, and two darker oils of specific gravity 0·867 and 0·961 respectively (Crell's Chem. Annal. i. 72). In 1817 Saussure published an account of his investigation of the native naphtha of Miano, in the Duchy of Parma, which was used at that time for lighting the streets of Genoa. He described it as being a transparent, yellow, thin liquid, 0·836 specific gravity, with a strong, persistent smell, separable by distillation into a colourless, lighter and more volatile portion, and a heavier, less volatile portion. The former he termed rectified naphtha. It had a specific gravity of 0·758, with only a slight evanescent odour, was entirely volatile at the ordinary atmospheric temperature, unalterable by exposure to light and air, and little acted on by strong acids. It mixed in all proportions with absolute alcohol, and dissolved in seven parts of alcohol of specific gravity 0·835. Caoutchouc macerated in this rectified naphtha without heat, swelled to at least thirty times its volume, but after forty-eight hours the naphtha contained only a seven-thousandth of its weight of caoutchouc. (Bibl. Univ. S. and A. iv. 116.)

In 1829 Unverdorben obtained from Persian petroleum similar products by distillation, and inferred that it consisted of a mixture of several oils together with a small quantity of a kind of solid fat (paraffin ?), resin, and an indifferent coloured substance. (Schweig. Jour. lvii. 243.)

Christison and Gregory in 1831 examined the petroleum of Rangoon. It was of a buttery consistence at ordinary temperatures, of a dark brown colour with a tinge of green, and a specific gravity of 0·880. They separated it by distillation into three different portions, and extracted paraffin from it. See PARAFFIN. (Trans. Roy. Soc. Edinb. xiii. 118, 124.)

Blanchet and Sell in 1833 obtained similar products from Persian petroleum, viz.: an oil of specific gravity 0·749, boiling at 94° C, and three oils boiling at 138°, 187° and 220° respectively. (Ann. Ch. Pharm. vi. 309.)

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In 1836 **Kobell** examined the petroleum from the Tegern Lake in Bavaria, known by the name of *Quirinus oil*, and separated from it a permanently liquid oil, and another which partly solidified when cooled to 6°. (J. pr. Chem. viii. 305.)

A thick brown petroleum from Niebylow in Galicia, examined by **Torosiwiecz**, had a specific gravity of 0·960 and became perfectly liquid only at 61°. Another kind from Truscawice was of specific gravity 0·890. (Repert. lv. 15; lxi. 398.)

**Hess** described the petroleum of Baku at the same time as having a specific gravity of 0·835, begining to boil at 140° and yielding by fractional distillation oils which had no fixed boiling point. (Pogg. Ann. xxxiv. 417.)

In 1840 **Pelletier** and **Walter** obtained by repeatedly rectifying that portion of the Miano petroleum which distilled between 130° and 270°, an oil which they called *naphtha* boiling at 83°—88°, to which they gave the formula $C^{14}H^{13}$; also an oil boiling at 115°, which they called *naphten* ($C^{16}H^{16}$), and an oil boiling at 19° which they called *naphtol* ($C^{24}H^{12}$), and they regarded these oils as the constituents of petroleum. J. Pharm. xxvi. 549.)

In 1848 and 1849 **Ure** and **Mansfield** examined a variety of mineral tar from a coal mine at Alfreton in Derbyshire. The specific gravity was 0·900, and it consisted chiefly of liquid oils boiling at temperatures above 300°, presenting in its characters some resemblance to the oil or tar distilled from bituminous shale. (Pharm. J. Trans. vii. 485; Chem. Soc. Qu. J. i. 249.)

Besides these investigations, several analyses of petroleum and of the products obtained from it by fractional distillation had been made, the result of which are given in the following table:

*Analyses of Petroleum and its products.*

| Kind of petroleum. | | Carbon. | Hydrogen. | Boiling point. | Authority. |
|---|---|---|---|---|---|
| Miano . . | Rectified products | 87·21 | 12·79 | . . | Saussure. |
| | | 85·65 | 13·31 | . . | |
| Persian . . | Rectified | 85·92 | 12·12 | . . | Dumas. |
| Persian . . | Rectified products | 83·88 | 14·29 | 94° | Blanchet and Sell. |
| | | 86·43 | 13·06 | 215° | |
| Baku . . | Rectified products | 79·82 to 85·85 | 13·20 to 14·51 | various | Hess. |
| Miano . . | Native | 85·58 | 13·17 | | |
| Miano . . | Rectified products | 85·30 | 13·40 | 100°—115° | Pelletier and Walter. |
| | | 84·50 | 13·40 | 115°—120° | |
| | | 85·80 | 13·30 | 120°—130° | |
| | | 85·50 | 13·40 | 140°—150° | |

These results did not advance the knowledge of the constitution of petroleum much beyond the point where it was left by **Unverdorben** in 1829, viz. that it was a varying mixture of hydrocarbon-compounds with pitchy or asphaltic substances dissolved in it to a greater or less extent, and elementary analysis was of little utility until some means had been found of separating the individual constituents more completely. (Schweigger's Journ. ix. 29.)

In 1857 **De la Rue** and **Müller** published the results of their examination of Rangoon petroleum, showing that it contained hydrocarbons of the benzene and olefine series, but consisted chiefly of compounds which were not acted upon by concentrated nitric or sulphuric acids. (Proc. Roy. Soc. viii. 221.)

**Eisenstück** examined the petroleum of Sehnde (Hanover) in 1858, and came to the conclusion that the oil obtained by distilling the crude petroleum with steam and boiling below 180°, consisted of a mixture of polymeric hydrocarbons $C^nH^{2n}$ homologous with ethylene, together with petrol $C^8H^{16}$. (Ann. Ch. Pharm. cxiii. 151.)

According to **Uelsman**, on the other hand, the products obtained by Eisenstück from this petroleum, and boiling between 135° and 145°, correspond with the formula $C^nH^{2n+2}$. (Ann. Ch. Pharm. cxiv. 279.)

**Freund** and **Pebal** examined Galician petroleum and came to the conclusion that it contains substances belonging to at least three different series, viz. homologues of ethylene, which are not acted upon by concentrated sulphuric acid at the ordinary temperature, homologues of benzene, and homologues of phenol. (Ann. Ch. Pharm. cxv. 19.)

The most important investigation of petroleum is that recently made by **Pelouze** and **Cahours** (Compt. rend. liv. 124, lvi. 505, lvii. 62). They operated upon the petroleum which has been brought in large quantity from Pennsylvania during the last few years, and succeeded in obtaining from it twelve distinct liquid hydrocarbons, which they consider to be homologues of marsh-gas (**Hydrides**, iii. 181), besides the solid hydrocarbons known under the name of paraffin (p. 342).

**Ronalds** has also shown that this petroleum probably contains the lower members of this series, corresponding to ethyl and trityl, and gaseous at ordinary temperatures (Chem. Soc. J. xviii. 529). **Schorlemmer** has stated that it also contains small quantities of benzene and its homologues, but these substances were not found by **Pelouze** and **Cahours**.

These results show that American petroleum consists chiefly of homologues of marsh-gas, and those which have been isolated present the following characters:—

| Formula. | Specific gravity. | Boiling point. | Vapour-density. | Authority. |
|---|---|---|---|---|
| $C^2H^6$ | gaseous | | | Ronalds. |
| $C^3H^8$ | gaseous | | | |
| $C^4H^{10}$ | 0·600 at 0° | 0° 4° | 2·110 | |
| $C^5H^{12}$ | 0·628 | 30° | 2·538 | Pelouze and Cahours. |
| $C^6H^{14}$ | 0·669 | 68° | 3·050 | |
| $C^7H^{16}$ | 0·699 | 92° 94° | 3·616 | |
| $C^8H^{18}$ | 0·726 | 116° 118° | 4·009 | |
| $C^9H^{20}$ | 0·741 | 136° 138° | 4·541 | |
| $C^{10}H^{22}$ | 0·757 | 160° 162° | 5·040 | |
| $C^{11}H^{24}$ | 0·766 | 180° 184° | 5·458 | |
| $C^{12}H^{26}$ | 0·776 | 196° 200° | 5·972 | |
| $C^{13}H^{28}$ | 0·792 | 216° 218° | 6·569 | |
| $C^{14}H^{30}$ | . . | 236° 240° | 7·019 | |
| $C^{15}H^{32}$ | . . | 255° 260° | 7·523 | |

American petroleum contains, besides these substances, other oils of much higher boiling point and of a specific gravity as high as 0·870; other kinds of petroleum also contain oils of still greater density, sometimes considerably above 0·900, but it has not yet been ascertained whether these are homologues of marsh gas. It is probable also that most kinds of petroleum contain olefines to some extent, or at least analogous oils which combine with concentrated sulphuric acid; but in most instances the homologues of marsh gas appear to constitute the chief bulk of petroleum.

The similarity existing between petroleum and the oily tar obtained by destructive distillation at temperatures below full red heat, as regards the chemical nature of the substances contained in these products, render it highly probable that petroleum has been formed by the decomposition of vegetal and animal remains, and that its origin is in some way connected with the formation of coal and other bituminous minerals from similar materials; but it is not evident what may have been the precise mode in which this change has taken place. The opinion which has generally been entertained as to the origin of petroleum, is that it has been formed by the action of heat upon coal beds situated beneath the earth's surface, that is to say, by a process of carbonisation or destructive distillation. The long recognised and obvious analogy between the various kinds of petroleum and the oily products resulting from the action of heat upon vegetal and animal substances has hitherto been the chief ground for that opinion, and the still closer resemblance which has since been found to exist between certain of these materials in the chemical nature of their constituents, would tend to increase the probability of its being correct, if there were not other facts which throw some doubt upon the formation of petroleum from coal by an actual process of destructive distillation. Thus for instance anthracite, which from its being the kind of coal containing the smallest amount of bituminous or volatilisable substance, would be most likely to be the residue of such a process, does not present any indications of having been exposed to such a temperature as is requisite for volatilising petroleum or for expelling the bituminous substance from other kinds of coal.

Reichenbach was induced to consider this subject from its connection with his study of the general phenomena of destructive distillation. The petroleum he examined did not contain paraffin, and observing some other differences between the oily tar he obtained by carbonising coal, and the specimens of petroleum he had examined, he concluded that there was an essential difference between these substances. Referring also to the fact that petroleum had never been met with where coal beds were subjected to the action of heat by underground combustion, he was led to doubt whether true petroleum originated in this way from the decomposition of coal. In the year 1833 he found that by distilling coal with water, an oily liquid was obtainable, to the extent of about $\frac{1}{320,000}$th part of the coal, which was clear, transparent, greenish-yellow, of specific gravity 0·836 and boiled at 167°, thus presenting great resemblance in these respects to the petroleum of Miano and of Persia, while at the same time it smelt like turpentine oil. Arguing from the assumed identity of petroleum and the oil thus obtained from coal, without decomposition as he supposed, together with the equally erroneous assumption of an essential dissimilarity between petroleum and the oily tar obtained by carbonising coal, he came to the conclusion that the commonly received opinion as to the origin of petroleum was erroneous, and was disposed to regard it, not as a product of the decomposition of coal, but as an actual constituent of coal, and in fact as being probably the turpentine oil of primæval pine forests. Hence he inferred that coal could not have been exposed to a temperature at all approaching that requisite for carbonisation, but that the petroleum it contained was expelled merely by the action of such a moderate heat as might prevail at no great depth below the surface. (*Schweig. Jour.* ix. 19.)

The discovery of paraffin and eupione in the petroleum of Rangoon showed that, so far as these could be regarded as being exclusively products of destructive distillation, Reichenbach's conclusion did not apply to all kinds of petroleum. Hence Gregory and Kobell adopted the opinion that petroleum containing these substances was at least a product of destructive distillation.

It has also been suggested somewhat vaguely that petroleum may have been formed by the combination of carbon with hydrogen at considerable depths below the earth's surface under the influence of volcanic heat and great pressure (Virlet, *Bulletin de la Soc. géol.* iv. 203; Verneuil, *ibid.* [2] i. 800; Lecoq, *Les Eaux minérales considerées dans leurs Rapports avec la Chimie et la Géologie*, 143 *et seq.*). It is possible that by the reaction of water and carbonaceous substances under certain conditions, hydrocarbons might be formed, and Berthelot's synthetic production of hydrocarbons (*Compt. rend.* xliii. 206) renders it probable that petroleum may in some instances have originated in a similar manner, though the precise nature of such modes of formation is not yet known. B. H. P.

**PETROSILEX** or *Adinoile.*—Compact impure felspar, like the base of porphyry. It differs from jasper, which it often resembles, in being fusible before the blowpipe. Specific gravity 2·60 to 2·66. (Dana.)

**PETUNTZE.** (*Peh-tun-tsz.*)—A felspathic rock consisting largely of quartz, used in China to mix with kaolin for the manufacture of porcelain.

**PETZITE.** Telluric silver. (See TELLURIUM.)

**PEUCEDANIN.** *Imperatorin.* $C^{12}H^{12}O^3$. (Schlatter, Ann. Ch. Pharm. v. 205.—Döbereiner, *ibid.* xxviii. 288.—Erdmann, J. pr. Chem. xvi. 42.—Bothe, *ibid.* xlvi. 371.—Wagner, *ibid.* lxii. 275; N. Jahrb. Pharm. ii. 83; xiv. 15.)—A neutral substance contained in the root of masterwort (*Imperatoria Ostruthium* L., *Peucedanum Ostruthium*, Koch), and of other umbelliferous plants of the peucedaneous tribe. It is prepared by exhausting the root of masterwort with boiling alcohol, evaporating the extract, washing the residue with water and with alcohol, and crystallising it from ether, which leaves undissolved a resinous substance wherewith the peucedanin is contaminated.

Peucedanin crystallises in light, transparent, colourless, shining prisms, grouped in tufts. It melts at 75° without loss of weight, and concretes again but slowly, yielding at first a transparent syrup which then solidifies to a waxy mass. It does not dissolve in *water*, either hot or cold; it is sparingly soluble in cold, more soluble in boiling *alcohol;* the solution has a persistently acrid taste, and does not act on vegetable colours. Peucedanin is very soluble in *ether*, and in *oils* both fixed and volatile.

Peucedanin gives by analysis from 69·6 to 71·1 per cent. carbon and 5·8 to 6·5 hydrogen, agreeing nearly with the formula $C^{12}H^{12}O^3$, which requires 70·6 per cent. carbon, 5·9 hydrogen and 25·5 oxygen. This formula is confirmed by the reaction of peucedanin with potash, whereby it is resolved into angelic acid and oreoselin (p. 215):

$$\underset{\text{Peucedanin.}}{C^{12}H^{12}O^3} + H^2O = \underset{\substack{\text{Angelic}\\\text{acid.}}}{C^5H^8O^2} + \underset{\text{Oreoselin.}}{C^7H^6O^2}.$$

Peucedanin is insoluble in *acids*, and is not acted upon at ordinary temperatures by *sulphuric, hydrochloric* or *acetic acid*. Strong *nitric acid* dissolves it with aid of heat, converting it either into nitropeucedanin or into oxypicric and oxalic acids. It decomposed by *chlorine* and *iodine*. The alcoholic solution is precipitated by certain *metallic salts*, the acetates of lead and copper for example.

*Nitropeucedanin*, $C^{12}H^{11}(NO^2)O^3$ (Bothe, *loc. cit.*), is produced by heating peucedanin to 60° with nitric acid of specific gravity 1·21. The resulting yellow solution solidifies on cooling to a crystallised mass which may be purified by crystallisation from alcohol. Nitropeucedanin forms colourless scales moderately soluble in alcohol and ether, nearly insoluble in water. It melts and decomposes at 100°. When heated to 100° in dry ammonia gas, or treated with ammonia and alcohol, it is converted into nitropeucedamide (probably $C^{12}H^{12}N^2O^4 = C^{12}H^{11}(NO^2)O^3 + NH^3 - H^2O$), which crystallises from boiling alcohol in shining rhomboïdal prisms very soluble in alcohol and ether, insoluble in water, and decomposed by weak acids or by caustic potash into nitropeucedanin and ammonia.

**PEUCYL.** Syn. with Terebilene.

**PHACOLITE.** A variety of chabasite from Leïpa in Bohemia (i. 844).

**PHACONIN.** An albuminous substance constituting the inner portion of the crystalline lens of the eyes of fishes (ii. 615).

**PHÆORETIN.** $C^{16}H^8O^7$?—A brown resinous substance obtained by Schlossberger and Döpping (Ann. Ch. Pharm. l. 207) from rhubarb-root. To prepare it the root is exhausted with alcohol of 60—80 per cent.; the evaporated extract is treated with water which dissolves only part of it; the undissolved portion, after being completely dried over the water-bath, is dissolved in the smallest possible quantity of alcohol of 80 per cent.; the solution is precipitated by ether, and the precipitate again treated with alcohol of 80 per cent., whereby it is separated into insoluble aporetin (i. 352) and a solution which when evaporated leaves phæoretin.

Phæoretin when dried and pulverised forms a yellowish-brown powder, having no taste of rhubarb, very slightly soluble in *water*, easily in *alcohol* and in *alkalis*, from which latter solutions it is precipitated with yellow colour by most mineral acids; it dissolves however in *acetic* and in *concentrated sulphuric acid*. Its compounds with the *alkalis* have a deep red-brown colour. When heated on platinum-foil it melts, giving off yellow vapours having a faint odour of rhubarb, and burns away without leaving a trace of ash. The solution of phæoretin in ammonia forms with *acetate of lead* a violet-red precipitate which appears to decompose during washing.

**PHÆOSIN** or **PHÆOSIC ACID.** A constituent of the pericarp of bay-berries (iii. 477).

**PHARMACOCALCITE.** Syn. with Olivenite.

**PHARMACOLITE.** Native calcic arsenate, occurring sometimes in distinct monoclinic prisms, but more frequently in delicate silky fibres, acicular crystallisations or stellate groups; also botryoïdal and stalactitic, sometimes massive. Hardness = 2—2·5. Specific gravity 2·64—273. It has a vitreous lustre, white or greyish colour, sometimes tinged with red from admixture of arsenate of cobalt; streak white. Translucent to opaque. Fracture uneven. Thin laminæ flexible. It is insoluble in water, but easily soluble in acids.

*Analyses.*—*a.* From Wettichen in the Black Forest (Klaproth, *Beiträge*, iii. 277). —*b.* From Andreasberg in the Harz (John. *Chem. Unters.* ii. 221).—*c.* Locality unknown (Turner, Pogg. Ann. v. 188).—*d.* From Glücksbrunn in the Thüringerwald (Rammelsberg, *ibid.* lxii. 150).

| | *a.* | *b.* | *c.* | *d.* |
|---|---|---|---|---|
| Arsenic anhydride . . | 50·54 | 45·68 | 79·01 | 51·58 |
| Lime . . . . . . | 25·00 | 27·28 | | 23·59 |
| Cobaltic and ferric oxides . | . . | . . | . . | 1·43 |
| Water . . . . . | 24·46 | 23·86 | 20·99 | 23·40 |
| | 100·00 | 96·82 | 100·00 | 100·00 |

These analyses lead to the formula $2Ca''O.As^2O^5.6H^2O$ (calc. 51·16 $As^2O^5$. 24·87 $Ca''O$ and 23·97 water), or $2Ca''HAsO^4.5H^2O$. The cobalt in the last is probably due to admixture of cobalt-bloom.

Pharmacolite is also found at St. Marie aux Mines in the Vosges, at Riechelsdorf and Bieber in Hessia, and at Joachimsthal in Bohemia; it occurs in association with arsenical ores of cobalt and silver.

*Picropharmacolite* from Riechelsdorf containing 46·97 per cent. $As^2O^5$, 24·65 lime, 3·22 magnesia, 1·00 cobalt-oxide, and 23·98 water, is probably pharmacolite having the lime partly replaced by magnesia.

**PHARMACOSIDERITE.** Syn. with Cube-ore (ii. 171).

**PHASEOLUS.** See Bean (i. 524).

**PHASEOMANNITE.** See Inosite (iii. 274).

**PHEASANT.** In the egg-shell of *Phasianus colchicus*, B. Wicke (Ann. Ch. Pharm. cxxv. 78) found 93·33 per cent. carbonate of calcium, 0·66 phosphate of magnesium, 1·37 phosphates, and 4·64 organic matter.

**PHENACITE** or **PHENAKITE.** A silicate of glucinum, occurring with emerald in Perm, Ilmen Mountains, and with quartz at Framont in Alsace, in rhombohedral crystals with scalenohedral and prismatic faces. R : R = 116° 40'; oR : R

= 142° 41′; length of principal axis = 0·66. ′ Cleavage imperfect parallel to R and ∞R2. Twins also occur, with face of composition parallel to ∞R. Hardness = 8. Specific gravity = 2·969. The crystals are transparent to opaque, colourless, or of bright wine-yellow colour inclining to red, and with vitreous lustre. Fracture similar to that of quartz. Infusible *per se* before the blow-pipe; forms colourless glasses with fluxes; melts to a milk-white bead with a small quantity of sodic carbonate, forms a tumefied infusible mass with a larger quantity. Not attacked by acids. A specimen from the Ilmen Mountains was found by Hartwall (Pogg. Ann. xxxi. 57) to contain 55·14 silica and 44·47 glucina (= 99·61; a specimen from Alsace analysed by Bischof (*ibid.* xxxiv. 525), gave 54·40 silica, 45·57 glucina, and 0·09 lime and magnesia—results agreeing nearly with the formula $2\overset{\prime\prime}{\mathrm{Be}}{}^{2}\mathrm{O}^{3}.3\mathrm{SiO}^{2}$ or $2\mathrm{G}''\mathrm{O}.\mathrm{SiO}^{2} = \acute{\mathrm{G}}{}^{2}\mathrm{SiO}^{4}$ (see GLUCINUM, ii. 849), which requires 53·96 silica, and 46·04 glucina.

**PHENAMEÏNE.** A name given to aniline-violet by Schenrer-Kestner (Jahresb. 1860, p. 728). who regards it as related to aniline in the same manner as naphthameïne (oxynaphthylamine) to naphthylamine.

**PHENAMYLOL.** PHENATE OR PHENYLATE OF AMYL. (See PHENOL, p. 391.)

**PHENATES.** See PHENYL, HYDRATE OF.

**PHENETOL.** PHENATE OF ETHYL.

**PHENGITE.** Syn. with MUSCOVITE.

**PHENIC ACID.** See PHENOL.

**PHENICINE.** A colouring matter produced by the action of nitrosulphuric acid (a mixture of strong nitric and sulphuric acids) on phenylic alcohol. The acid is added in successive portions to crystallised phenylic alcohol, the mixture being cooled after each addition, as long as red vapours continue to escape. The acid liquor is then poured into a large quantity of water, and the resulting precipitate is washed with water and dried.

Phenicine is a brown amorphous powder, sparingly soluble in water, easily soluble in alcohol, ether and acetic acid. Alkalis likewise dissolve it easily, imparting a fine violet-blue colour, which however is changed to brown by the least excess of acid. It dissolves also in lime-water. It melts and turns black at a moderate heat. It is a mixture of two colouring matters, one yellow, the other black, both of which however possess the same tinctorial properties.

Phenicine, like the aniline colours, dyes silk and wool without the intervention of a mordant. A piece of silk or wool dyed with phenicine acquires a fine garnet-red colour on immersion in a solution of chromate of potassium, or better, of chromate of copper acidulated with sulphuric acid. Nitrate of copper produces the same effect but with less intensity. Cotton mordanted with stannate of soda or with tannin easily absorbs phenicine, and acquires a deep purple colour on subsequent immersion in hot potassic chromate; but the colour is changed to blue by alkalis, and easily destroyed by soap.

Strong nitric acid converts phenicine into a resinous paste which dissolves in ammonia, forming a brown solution which dyes silk and wool somewhat like archil. (E. Dolfus, Bull. Soc. Chim. 1865, i. 226.)

**PHENOIC ACID.** $C^6H^4O^2$.—An acid isomeric with collinic acid (i. 1083), produced by heating a solution of benzene in a slight excess of fuming sulphuric acid to 100°, then diluting with water, and gradually adding small pieces of acid potassic chromate. The distillate contains phenoic acid, partly dissolved, partly floating as an oil, and in crystals. It is distinguished from collinic acid by its greater solubility in hot water. Its *silver-salt* contains $C^6H^3AgO^2$. (Church, Chem. Soc. J. xiv. 52.)

An acid of the same composition and doubtless identical with the preceding is obtained by distilling coal-tar (containing toluene, xylene and pseudocumene) with dilute nitric acid. This acid melts at about 60°, but occasionally remains liquid at ordinary temperatures, especially when not quite pure. It has an acrid taste, is heavier than water, mixes in all proportions with alcohol, is only slightly soluble in cold water, more soluble in boiling water. From a saturated hot solution it separates while cooling as a heavy oil which sometimes solidifies immediately. It is slightly volatile, covering itself with beautiful crystallisations even at ordinary temperatures. When boiled with water, it volatilises to a considerable extent. It can be distilled *per se* without decomposition, and forms well crystallised salts with the alkalis. (De La Rue and Müller, Chem. Soc. J. xiv. 54.)

*Nitrophenoic acid*, $C^6H^3(NO^2)O^2$, is produced by oxidising nitrobenzene with sulphuric acid and potassic chromate. It crystallises in nacreous laminæ, has a strong acid reaction, melts without decomposition, dissolves in boiling water, and yields crystallisable salts. (Church.)

**PHENOL.** $C^6H^6O = \left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O$. *Hydrate of Phenyl. Phenylic alcohol. Phenic acid. Carbolic acid. Coal-tar creosote.* (Runge, Pogg. Ann. xxxi. 69; xxxii. 308.—Laurent, Ann. Ch. Phys. [3] iii. 195.—Williamson and Scrugham, Chem. Soc. J. vii. 232).—This compound is contained in considerable quantity in coal-tar (Runge, Laurent), and is produced by the dry distillation of salicylic acid, either alone or in contact with caustic lime or baryta (Gerhardt, Rev. scient. x. 210):

$$C^7H^6O^3 = C^6H^6O + CO^2.$$

It is also formed in the dry distillation of gum-benzoin (E. Kopp), of the resin of *Xanthorrhæa hastilis*, of quinic acid (Wöhler), of chromate of pelosine (Bödeker, p. 372), and is found in small quantity among the products obtained by passing the vapour of alcohol or acetic acid through a red-hot tube (Berthelot). It is to phenol that castoreum owes its peculiar odour (Wöhler). The urine of the cow, of the horse, and of man contain sensible quantities of phenol (Städeler, Ann. Ch. Pharm. lxvii. 360; lxxvii. 17). Commercial creosote often consists almost entirely of phenol, but the true creosote, obtained by the distillation of wood, is a totally different substance (ii. 103).

*Preparation.* 1. From *Coal-tar.*—The tar is distilled till anthracene begins to pass over; the resulting oil is rectified, collecting apart the portion which distils over between 150° and 200°; this portion is mixed with saturated potash-ley and pulverised hydrate of potassium, whereby it is immediately converted into a white crystalline magma; this substance is dissolved in hot water; the oil which rises to the surface is removed; the lower alkaline liquid is neutralised with hydrochloric acid; the impure hydrate of phenyl, which rises to the surface as an oil, is washed with a little water, digested over chloride of calcium, rectified several times, and gradually cooled to −10° in a closed vessel; and the resulting crystals of pure phenol are freed from the remaining fluid portion by inverting the bottle over another, care being taken to exclude the air, which might give up water to the crystals (Laurent). The tedious fractional distillations evolved in this process may be considerably abridged by introducing into the portions which boil between 186° and 188°, a few crystals of pure phenol; a large portion of the liquid then solidifies after a while in colourless needles, which, when separated from the liquid, distil at 184° and yield a sublimate of pure phenol. (Williamson and Scrugham.)

Gladstone (Chem. News, ii. 98) recommends placing good commercial carbolic acid for some days in contact with a lump of chloride of calcium and then leaving the phenol to crystallise out in a freezing mixture. He is of opinion that the cresol or cresylic alcohol likewise present in crude carbolic acid is converted into phenol by contact with chloride of calcium or chloride of zinc.

2. From *Salicylic acid.*—Crystallised salicylic acid is strongly and quickly heated in a glass retort either alone or mixed with pounded glass or quicklime. Phenol then passes into the receiver and crystallises on cooling almost to the last drop. The phenol thus obtained appears however to differ in some of its properties from that obtained from coal-tar, inasmuch as it crystallises more readily and reacts somewhat differently with pentachloride of phosphorus (p. 390).

*Properties.*—Phenol crystallises at ordinary temperatures in long colourless needles apparently belonging to the trimetric system, and having a specific gravity of 1·065 at 18° (Laurent), 1·0627 (Scrugham). It melts at 34°—35°, and boils at 187°—188° (Laurent); 184° (Scrugham). The crystals of phenol obtained from coal-tar deliquesce easily to an oil by taking up a mere trace of water (Laurent); a lump of chloride of calcium causes the oil to solidify immediately (Gerhardt). Phenol produced by decomposition of salicylic acid is much less deliquescent than that obtained from coal-tar (Watts). Phenol does not redden litmus. It smells like wood-tar creosote, and attacks the skin like that substance. Its aqueous solution coagulates albumen; it unites with certain animal substances and preserves them from decomposition, even removing the fetid odour from meat and other substances already in a state of decomposition. Fish and leeches die when immersed in the aqueous solution, and their bodies subsequently dry up on exposure to the air, without putrefying.

Phenol is but sparingly soluble in *water*, but dissolves in all proportions in *alcohol, ether* and strong *acetic acid*. When shaken up with ¼ pt. of water and exposed to a temperature of 4°, it takes up water and forms a hydrate $2C^6H^6O.H^2O$, which crystallises readily in large six-sided prisms belonging to the trimetric system, and melting at 16°. (Calvert, Chem. Soc. J. xviii. 66.)

Phenol may be distilled without alteration over melted phosphoric acid, also over caustic potash, baryta, or lime.

*Decompositions.*—1. Phenol passed through a red-hot tube undergoes very little decomposition, yielding however a small quantity of naphthalene (Hofmann).—2. Strong *sulphuric acid* dissolves it with great rise of temperature, but without colora-

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tion, forming phenyl-sulphuric acid. It reduces *mercuric oxide* at the boiling heat, separates metallic *silver* from the nitrate, and reduces *peroxide of lead* to protoxide. Heated with *arsenic acid*, it forms a yellow substance called xanthophenic acid. (F. Fol, Rép. Chim. app. iv. 179.)

3. Strong *nitric acid* attacks phenol with great violence, each drop as it comes in contact with the phenol, hissing like red-hot iron plunged into water: the product formed at the boiling heat is trinitrophenic or picric acid, $C^6H^3(NO^2)^3O$; a less energetic reaction produces mono- or di-nitrophenic acid (p. 393).

5. *Chlorine* and *bromine* likewise act upon phenol, forming substitution-products possessing acid characters (pp. 391, 392).

6. When chlorine is passed into phenol which is kept cool; and the product treated with three times its weight of strong nitric acid, dinitrochlorophenic acid, $C^6H^2Cl(NO^2)^2O$, is produced. (Griess, Ann. Ch. Pharm. cix. 286.)

7. Phenol is scarcely, if at all, attacked by *iodine*, but with *chloride of iodine* it forms mono- and di-iodophenic acids. (Schützenberger and Sengenwald, Compt. rend. liv. 197).

8. *Chloride of thionyl*, $SOCl^2$, acts strongly on phenol dissolved in ether, eliminating considerable quantities of hydrochloric and sulphurous acids, but does not appear to form any phenylic sulphate.

9. A mixture of *hydrochloric acid and potassic chlorate* converts phenol, first into trichlorophenic acid, and subsequently into perchloroquinone or chloranil, $C^6Cl^4O^2$. (See QUINONE, DERIVATIVES OF.)

10. *Pentachloride of phosphorus* converts phenol into chloride and phosphate of phenyl. With phenol from coal-tar the products are chloride of phenyl and triphenylic phosphate (Williamson and Scrugham), perhaps thus:

$$5(C^6H^5.H.O) + 2PCl^5 = 2C^6H^5Cl + P(C^6H^5)^3O^4 + PCl^3O + 5HCl;$$

but with phenol from salicylic acid, an acid phosphate is obtained, which forms salts with metallic bases, and probably consists of diphenylic phosphate:

$$5(C^6H^5.H.O) + 2PCl^5 = 3C^6H^5Cl + P(C^6H^5)^2HO^4 + PCl^3O + 4HCl.$$

This acid phosphate crystallises much more easily than the neutral triphenylic phosphate (H. Watts, *unpublished experiments*). See PHOSPHORIC ETHERS.

11. With *chloride of benzoyl*, phenol forms phenylic benzoate, $C^7H^5(C^6H^5)O^2$ (i. 553).

12. *Cyanic acid* vapour passed into perfectly dry phenol converts it into allophanate of phenyl, $C^2H^3(C^6H^5)N^2O^3$, which crystallises from hot alcohol in slender, unctuous, tasteless, inodorous crystals, insoluble in cold water, resolved at 150° into phenol and cyanuric acid, and converted by alcoholic potash into allophanate of potassium, by baryta-water into allophanate of barium. (Tuttle, Jahresb. 1857, p. 451.)

13. Phenol does not dissolve in aqueous *ammonia*, but it absorbs ammonia gas, and the solution when heated in a sealed tube is partly converted into water and aniline:

$$C^6H^6O + NH^3 = H^2O + C^6H^7N.$$

14. Phenol is attacked by *potassium* or *sodium*, slowly at first, more quickly when aided by a gentle heat, hydrogen being evolved, and phenate of potassium or sodium produced. (Laurent.)

15. When *carbonic anhydride* is passed into pure phenol gently warmed, and *sodium* is added by small portions, hydrogen is evolved and salicylate of sodium is formed. The reaction is the converse of that by which phenol is produced from salicylic acid. (Kolbe and Lautemann, Jahresb. 1859, p. 309; 1860, p. 291.)

PHENATES—1. *Metallic.*—Phenol unites with the stronger bases, but the compounds are very unstable and difficult to obtain in definite form. Indeed phenol has, in properties as well as in composition, the character of an alcohol rather than that of an acid. It dissolves in caustic potash, but the quantity dissolved does not increase in proportion to the quantity of potash present (Calvert, Chem. Soc. J. xviii. 68); it also dissolves carbonate of potassium, but without expelling carbonic acid. Phenol does not unite with the acid sulphites of the alkali-metals, and therefore does not behave like an aldehyde, in which character Gmelin is inclined to regard it (*Handbook*, xi. 146).

*Phenate of potassium* is produced, as already observed, by heating phenol with potassium; also by direct combination of solid potash with phenol. The oily liquid formed in either case deposits the potassium-salt on cooling in white needles very soluble in alcohol, ether, and water, and decomposed by mineral acids with separation of phenol. (Laurent.)

*Phenate of barium*, $C^{12}H^{10}Ba''O^2.3H^2O$, is obtained by boiling phenol with baryta-water and evaporating in vacuo, as a crystalline crust containing 42·48 per cent. baryta.

*Phenate of lead*, obtained by boiling phenol with litharge and adding a few drops of alcohol to the product, is a white mass containing, according to Calvert, $C^{12}H^{12}O^2.2Pb''O$ or $C^{12}H^{10}Pb''O^2.Pb''H^2O^2$. It is slightly soluble in hot alcohol, and separates on cooling. With basic acetate of lead, phenol forms precipitates of uncertain composition. (Calvert.)

2. *Alcoholic Phenates. Phenic Ethers.*—α. *Methylic Phenate* or *Anisol* has been already described under the latter name, together with its bromo- and nitro-derivatives, and the bases formed by the action of reducing agents on the latter (i. 304—306).

β. *Ethylic Phenate*, *Phenetol* or *Salithol*, $C^8H^{10}O = C^6H^5(C^2H^5)O$ (Cahours, Ann. Ch. Phys. [3] xxvii. 463.—Baly, Ann. Ch. Pharm. lxxiii. 208).—This compound is obtained by the dry distillation of perfectly anhydrous ethyl-salicylate of barium, the oily distillate being purified by washing with warm alkaline ley, digesting with fused chloride of calcium, and rectification. It is a colourless, mobile liquid, lighter than water, having an agreeable aromatic odour, insoluble in water, very soluble in alcohol and ether, boiling at 172°. It is not altered by potash. *Sulphuric acid* converts it into a sulpho-acid forming a soluble barium-salt. With *chlorine* and *bromine* it forms crystallisable products. It is strongly attacked by fuming *nitric acid*, the products varying in composition according to the proportions used; with a small quantity of the acid a reddish-brown oil is obtained, probably consisting of mononitrophenetol; but on boiling ethylic phenate with an excess of the fuming acid, dinitrophenetol, $C^8H^8(NO^2)^2O$, is obtained (see page ).

γ. *Amylic Phenate* or *Phenamylol*, $C^{11}H^{16}O = C^6H^5(C^5H^{11})O$ (Cahours, Compt. rend. xxxii. 61). Obtained by heating amylic iodide with potassic phenate to 100°—120° in a sealed tube. It is a limpid colourless oil, lighter than water, having a pleasant aromatic odour, and boiling between 224° and 225°. It is attacked with great violence by fuming nitric acid, forming a heavy oil, which, when treated with alcoholic sulphide of ammonium, yields a crystallised base (amyl-nitrophenidine, or nitro-phenamylidine) capable of forming crystallisable salts. Phenamylol dissolves in sulphuric acid, forming a red liquid, which gives no precipitate with water, but forms a crystallisable barium-salt.

**PHENOL, DERIVATIVES OF.** One, two, or three of the hydrogen-atoms in phenol may be replaced by bromine, chlorine, iodine, or nitryl, forming compounds which have more and more of an acid character as the substitution is more complete.

### 1. *Bromophenol* or *Bromophenic Acids.*

**Monobromophenic acid.** $C^6H^5BrO$. *Bromophenasic acid* (Cahours, Ann. Ch. Phys. [3] xii. 102).—Obtained, as a colourless oil, by distilling bromosalicylic acid with a mixture of sand and carbonate of barium.

**Dibromophenic acid.** $C^6H^4Br^2O$. *Bromophenesic acid.*—Obtained in like manner from dibromosalicylic acid, as an oil which crystallises on cooling. (Cahours, *loc. cit.*)

**Tribromophenic acid.** $C^6H^3Br^3O$. *Bromophenisic* or *Bromindoptic acid*, (Laurent, Ann. Ch. Phys. [3] iii. 211.—Erdmann, J. pr. Chem. xxii. 272.—Cahours, *loc. cit.*).—Phenol immersed in excess of bromine becomes strongly heated, gives off hydrobromic acid, and solidifies on cooling to a brown mass, which must be boiled with water and ammonia; the solution subsequently filtered from a small quantity of brown matter, and decomposed by hydrochloric acid; and the thick precipitate of tribromophenic acid washed on a filter (Laurent).—2. Tribromosalicylic acid, distilled two or three times with fine sand and a small quantity of baryta, also yields tribromophenic acid (Cahours).—3. When indigo is decomposed by bromine-water and the product subsequently distilled with potash, bromaniline passes over, and tribromophenic acid remains behind. (Erdmann.)

Tribromophenic acid crystallises by fusion or sublimation, or from solution, in delicate white needles, or right rhombic prisms, having the acute lateral edges truncated. Angle $\infty P : \infty P = 128°$; $\infty P : \infty \breve{P} \infty = 116°$. It is fusible, crystallises on cooling, and may be distilled without decomposition; smells like trichlorophenic acid. It is somewhat less soluble in *alcohol* than the latter. When boiled with *nitric* acid, it forms at first a reddish resin, which gradually disappears, and on evaporation, crystals of picric acid are obtained.

The tribromophenates, when heated to redness, generally leave a metallic bromide, and give off tribromophenic acid (?).

The *ammonium-salt* crystallises in needles. Its solution forms with concentrated chloride of *barium* or chloride of *strontium*, a precipitate composed of needles; with *neutral acetate of lead*, a white precipitate; with *cupric acetate*, a red-brown precipitate, soluble in alcohol; and with *nitrate of silver*, an orange-yellow precipitate.

*Substance isomeric with tribromophenic acid.*—A concentrated aqueous solution of salicylate of potassium, mixed with a small quantity of potash, and then with a large quantity of bromine, becomes heated and decolorised, gives off carbonic anhydride, and soon deposits a kermes-brown substance, which is insoluble in water, ammonia, cold potash, and alcohol, but dissolves with extreme facility in ether; it contains, after washing and drying, 22·19 per cent. C, 71·8 Br, and 0·88 H; and, when heated, gives off white vapours, which condense into delicate white needles of tribromophenic acid. (Cahours, Ann. Chim. Phys. [3] xiii. 43.)

### 2. *Chlorophenols* or *Chlorophenic Acids.*

**Dichlorophenic acid.** $C^6H^4Cl^2O$. *Dichlorocarbolic acid. Chlorophenesic acid.* (Laurent, Ann. Ch. Phys. [2] lxiii. 27; [3] iii. 210.)—This acid is produced: 1. By the comparatively feeble action of chlorine on phenol.—2. By distilling dichlorosalicylic acid with fine sand and a small quantity of lime or baryta. It may be prepared from the impure phenol which passes over between 170° and 200° in the rectification of coal-tar naphtha. For this purpose chlorine is passed through the yellowish oily distillate for a day, and the liquid, cooled to − 10°, is strained through linen to separate the naphthalene which has crystallised out: chlorine is then again passed for two days through the liquid, which is then cooled to 0°, decanted from crystallised hydrochlorate of dichloronaphthalene, and distilled (whereupon it froths up considerably, giving off a large quantity of chlorine, and afterwards hydrochloric acid) till the thick black residue exhibits considerable intumescence (tetrachloronaphthalene then subliming in needles); the distillate is shaken up in a bottle with oil of vitriol as long as hydrochloric acid continues to escape; the rose-coloured oil of vitriol (which deposits a stinking substance when neutralised), is removed by a syphon; the remaining oil is washed with a large quantity of water, and mixed in the flask with ammonia, with which it solidifies completely into a white mass, with slight rise of temperature; this mass is boiled with water; the solution decanted hot from a brown oil, which is again to be treated with ammonia, and then with hot water to remove the acids completely; the hot filtered aqueous solutions, containing di- and trichlorophenate of ammonium, are mixed by drops with dilute nitric acid till a slight turbidity is produced; the liquid is filtered from the red-brown precipitate; the filtrate precipitated with a slight excess of nitric acid; the white precipitate, which is gelatinous at first, but afterwards curdy, and consists of fine needles, collected on a filter, and distilled after washing, pressing, and drying; and the distillate boiled with a slight excess of aqueous carbonate of sodium, which leaves behind the oily dichlorophenic acid, while the crystalline trichlorophenic acid is precipitated from the filtrate by nitric acid, and purified by distillation. (Laurent.)

Dichlorophenic acid is an oil which volatilises without residue, has a peculiar odour, is insoluble in *water*, but dissolves very easily in *alcohol* and *ether*. With aqueous *ammonia* it immediately solidifies into a crystalline mass, which, however, on exposure to the air, gives off ammonia and becomes oily, but solidifies when again treated with ammonia. The solid salt is soluble in water.

**Trichlorophenic acid.** $C^6H^3Cl^3O$. *Trichlorocarbolic, Chlorophenisic* or *Chlorindoptic acid.* (Laurent, Ann. Ch. Phys. [2] lxiii. 27; [3] iii. 497.)—This acid is formed by the action of chlorine on phenol or dichlorophenic acid; of chlorine in presence of water, on indigo, aniline, and saligenin; and of a mixture of hydrochloric acid and potassic chlorate, continued for a short time only, on phenol.

It may be prepared: 1. From *coal-tar naphtha*, either by the method just described with reference to dichlorophenic acid, or better, by repeatedly distilling the commercial oil obtained from coal-tar, collecting apart the portion which boils between 170° and 190°; separating it out from the naphthalene which crystallises out in the cold; passing chlorine gas through it for a day or two according to the quantity; distilling it till nothing but a carbonaceous residue is left (whereupon hydrochloric acid is given off and a very offensive odour emitted), the receiver being changed at certain stages of the process, and the first and last portions of the distillate set aside; passing chlorine through the middle distillate till it solidifies into a crystalline paste; purifying this mass from adhering oil by spreading it on paper and pressing it; dissolving the crystalline mass—which, besides the trichlorophenic acid, likewise contains a little oil and crystalline chloralbin ($C^6Cl^2H^8$)—in boiling water containing ammonia; filtering; dissolving in water the trichlorophenate of ammonium which has crystallised out on cooling; mixing the solution with hydrochloric acid to precipitate the trichlorophenic acid; and purifying this product by washing, drying, and distillation. (Laurent.)

2. *From Saligenin.*—When chlorine gas is passed through an aqueous solution of saligenin, the bottle being frequently closed and shaken, the liquid immediately becomes turbid, then deposits a yellow, afterwards reddish, and finally orange-yellow crystalline resin, and a white, bulky, crystalline precipitate. To free the entire precipitate from a closely adhering reddish oil, it is distilled three or four times with oil of vitriol, which

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carbonises the oil, with evolution of sulphurous and hydrochloric acids, and ultimately pure trichlorophenic acid distils over. (Piria.)

*From Indigo.*—When chlorine-gas is passed through water in which indigo is suspended, and the yellowish-red magma is distilled, with cohobation of the watery distillate, a crystalline sublimate is obtained, consisting of trichloraniline and trichlorophenic acid; and when this mixture is distilled with potash, the trichloraniline passes over, while crystallised trichlorophenate of potassium remains behind, mixed with free potash. This residue is pressed, exposed to the carbonic acid in the air, dissolved in the smallest possible quantity of boiling alcohol, and left to crystallise after filtration; and from the aqueous solution of the capillary crystals thus obtained, the trichlorophenic acid is precipitated by acids. (Erdmann.)

Trichlorophenic acid crystallises from solution—best from rock-oil—or by sublimation, in very slender silky needles or in right rhombic prisms, generally exhibiting the combination $\infty P . \infty \breve{P}\infty . oP$. Angle $\infty P : \infty P = 110°$; $\infty P : \infty \breve{P}\infty = 145°$. It melts at 44° (Laurent); 58° (Piria), and solidifies on cooling to a radiated mass of needles. It boils at 250° and distils without alteration. It has a very penetrating and persistent odour, and is easily set on fire, burning with a green-edged smoky flame and emitting hydrochloric acid vapours. It is insoluble or nearly so in *water*, but dissolves in all proportions in *alcohol* and *ether*; it dissolves also in *oils*, both fat and volatile; easily also in warm *fuming sulphuric acid*, with which it solidifies to a mass of needles on cooling. Boiling *nitric acid* converts it into a reddish substance (called *chlorophenyl* by Laurent and containing 37·8 per cent. C, 1·92 H, and 54·3 Cl), which becomes crystalline by prolonged ebullition. Trichlorophenic acid heated with *chlorate of potassium* and *hydrochloric acid* is converted into perchloroquinone or chloranil:

$$C^6H^3Cl^3O \quad + \quad Cl^4 \quad + \quad O \quad = \quad C^6Cl^4O \quad + \quad 3HCl.$$

The trichlorophenates give off trichlorophenic acid by dry distillation, leaving a metallic chloride and charcoal. They burn with a smoky green-edged flame. Nitric acid added to these solutions, throws down the trichlorophenic acid in the form of a bulky mass. (Laurent.)

*Ammonium-salt.*—The solution of the acid in aqueous ammonia, yields needles which have a slight alkaline reaction, and sublime completely when exposed to the heat of the sun, but by dry distillation in a retort, are partially resolved into nitrogen, ammonia, trichlorophenic acid, dichlorophenic acid, and sal-ammoniac. The salt dissolves very sparingly in cold, very easily in hot water, or in water containing alcohol (Laurent). The *potassium* and *sodium-salts* form very slender needles.

The *barium-salt* is obtained as a white gelatinous precipitate on mixing a concentrated solution of the ammonium-salt with chloride of barium. Dilute solutions yield no precipitate, but if both solutions are boiling and concentrated, the trichlorophenate of barium separates in long needles.

The ammonium-salt throws down from concentrated (not from dilute) solutions of *chloride of calcium*, and likewise of *alum*, a white jelly; it precipitates *neutral acetate of lead* and *ferrous-salts*, white; *ferric salts*, reddish; *cobalt-salts*, reddish; *nickel-salts*, greenish; *cupric salts*, brown-red (dark purple violet, according to Erdmann and Hofmann), the precipitate dissolving with brown colour in hot alcohol, and crystallising on cooling in brown, shining, oblique rectangular prisms; *mercurous nitrate*, white, according to Erdmann; *mercuric chloride*, yellowish-white, curdy; and *nitrate of silver*, lemon-yellowish. The silver-salt thus obtained has the composition $C^6H^2AgCl^3O$. (Laurent.)

**Pentachlorophenic acid.** $C^6HCl^5O$. *Perchlorophenic, Perchlorocarbolic, Chlorophenusic* or *Chlorinated Chlorindoptic acid.* (Erdmann, J. pr. Chem. xxii. 272.—Laurent, Ann. Ch. Phys. [3] iii. 497.)—Produced by the action of chlorine on an alcoholic solution of trichlorophenic acid, chlorisatin, or dichlorisatin (iii. 406, 408). To prepare it, chlorine is passed into boiling alcohol of 80 per cent. containing chlorisatin or dichlorisatin in suspension or solution, till the thick oily precipitate thereby produced no longer increases. This precipitate is washed with water (to extract sal-ammoniac), and exhausted when cold with alcohol, which leaves undissolved the greater part of the perchloroquinone (chloranil) formed at the same time; the alcoholic solution is mixed with water which throws down a resinous substance, and this precipitate is dissolved in hot caustic potash. The solution thus obtained deposits on cooling, crystals of potassic pentachlorophenate, which is purified by recrystallising it several times from potash, wherein it is but slightly soluble.

Pentachlorophenic acid precipitated from the potassium-salt by hydrochloric acid forms white flocks, which when dissolved in rock-oil, separate in right rhombic prisms, truncated on the acute lateral edges. Angle $\infty P : \infty P$ = about 110°. It is less fusible and less volatile than trichlorophenic acid, but may be sublimed in long needles by distillation with water. Its odour is like that of trichlorophenic acid, but more agreeable.

*Pentachlorophenate of Ammonium* forms groups of laminæ, sparingly soluble in water. The *potassium-salt* crystallises in needles or rhombic prisms. The solution does not precipitate the salt of *calcium* or *magnesium*; but forms a white flocculent precipitate with *chloride of barium*; brownish-white with *iron-salts*; reddish with *nitrate of cobalt*; greenish with *nitrate of nickel*; dark violet-purple with *cupric sulphate*; white flocculent with *mercuric nitrate* or *chloride*; yellow with *nitrate of silver*. The silver-salt thus formed contains $C^6AgCl^5O$.

### 3. *Iodophenols or Iodophenic Acids.*

The mono- and di-iodated compounds are produced, with copious evolution of hydrochloric acid, by the action of chloride of iodine on phenol. The solution of the residue in soda-ley yields, on addition of hydrochloric acid, a greyish-white viscid body which when heated under the ordinary atmospheric pressure, is resolved into a large quantity of iodine and rosolic acid, but when distilled in a vacuum, yields liquid mono- and di-iodophenol containing a small quantity of rosolic acid.

*Mono-iodophenol*, $C^6H^5IO$, is colourless, syrupy, insoluble in *water*, soluble in *alcohol* and *ether*, and forms with alkalis, crystallisable salts which are soluble in pure water, but insoluble in strong potash-ley.

*Di-iodophenol*, $C^6H^4I^2O$, is a colourless solid, which melts at about 110°, dissolves sparingly in water, and crystallises from hot dilute alcohol in slender flattened needles. It dissolves in *alcohol*, *ether*, and *alkalis*, forming with the latter, compounds which are soluble in water, but insoluble in strong potash-ley. When heated it gives off iodine and leaves rosolic acid. (Schützenberger and Sengenwald, Compt. rend. liv. 197.)

### 4. *Nitrophenols* or *Nitrophenic Acids.*

**Nitrophenic acid,** $C^6H^5(NO^2)O$. *Nitrocarbolic acid.* (Hofmann, Ann. Ch. Pharm. lxxv. 358; ciii. 247.—Fritzsche, Petersb. Acad. Bull. xvi. 11; J. pr. Chem. lxxiii. 293; Jahresb. 1857, p. 453.)—This acid is produced by the action of nitric acid on phenol, and by that of nitrous acid upon aniline. When nitric oxide gas is passed into a solution of aniline in strong nitric acid, a brown resinous mixture is formed containing crystalline nitrophenic acid, a brown amorphous substance, and a trace of phenol. Nitrophenic acid is also obtained in small quantity by distilling aniline with dilute nitric acid. (Hofmann.)

*Preparation from Phenol.*—To obtain nitrophenic acid free from di- and trinitrophenic acids, the action of the nitric acid must be carefully regulated. For this purpose Hofmann mixes phenol and the strongest nitric acid by small quantities, keeping the whole well cooled by a freezing mixture; then adds water, and distils the resulting mixture of water, oil and resin; or he distils a homogeneous mixture of phenol and water with ordinary nitric acid, whereupon the liquid suddenly turns brown, a resin separates from it, and yellow drops of nitrophenic acid pass over with the watery distillate and soon solidify in the crystalline form. Fritzsche dissolves 2 pts. of pure phenol in 100 pts. boiling water, adds 3 pts. of fuming nitric acid of specific gravity 1·51, and distils. At first the nitrophenic acid acid passes over in oily drops which ultimately solidify; afterwards as an aqueous solution, the first portions of which deposit needle-shaped crystals of nitrophenic acid when cooled to 0°. The nitrophenic acid separated from the accompanying liquid is purified by redistillation with water and recrystallisation from alcohol and ether.

*Properties.*—Nitrophenic acid crystallises in prisms of 132° 49′, and 47° 11′, having their acute and obtuse edges much truncated, but whether they are trimetric or monoclinic could not be determined, on account of the imperfect development of the terminal faces (Kokscharow, Petersb. Acad. Bull. xvii. 273). It has a light yellow colour, an aromatic not unpleasant odour, and sweet aromatic taste; melts at 42°, and solidifies again at 26° (Hofmann); melts at 45°, and solidifies at the same temperature (Fritzsche); boils at 216° (Hofmann), at 214° (Fritzsche). It dissolves easily in *alcohol* and *ether* (Hofmann, Fritzsche), and separates therefrom by slow evaporation in yellow needles (Hofmann); sparingly in *water* (Hofmann), sparingly in cold, more easily in hot water (Fritzsche); easily in *benzene* and *sulphide of carbon* (Fritzsche). The solutions have an acid reaction. By *sulphuric acid* it is converted, slowly when dissolved in ammonia, easily when dissolved in potash or soda, into amidophenol, $C^6H^5(NH^2)O$. (Hofmann.)

The nitrophenates are scarlet or orange-coloured according to the quantity of water which they contain.

The *ammonium-salt* separates on cooling from a solution of nitrophenic acid in warm

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aqueous ammonia, in orange-yellow laminar crystals, which quickly give off ammonia even when exposed to the air in the moist state. The dry salt is more easily prepared by passing dry ammonia-gas into an ethereal solution of nitrophenic acid, whereupon it separates in laminar crystals, which, after being quickly washed with ether and pressed between paper, may be preserved in a well-closed vessel (Fritzsche). The *potassium-salt* is obtained by dissolving an excess of nitrophenic acid in a solution of caustic potash in alcohol of 90 per cent. and crystallises from the concentrated liquid on cooling in flat orange-red crystals containing $2C^6H^4K(NO^2)O.H^2O$; between 120° and 130° they give off their water and turn red. The same salt may be obtained in orange-coloured needles by the process given by Hofmann for the preparation of the sodium-salt (Fritzsche). The *sodium-salt*, $C^6H^4Na(NO^2)O$, is obtained in scarlet crystals by adding soda in excess to nitrophenic acid, exposing the compound to the air till all the free soda is converted into carbonate, and recrystallising from absolute alcohol. (Hofmann, Fritzsche.)

The *barium-salt*, $C^{12}H^8Ba''(NO^2)^2O^2$, separates in scarlet tabular crystals on boiling baryta-water with excess of nitrophenic acid till the excess is driven off, and leaving the filtrate to cool (Fritzsche).—The *strontium-salt* prepared in like manner forms orange-coloured needles containing $C^{12}H^8Sr''(NO^2)^2O^2.3H^2O$ (Fritzsche).—The *calcium-salt* crystallises in orange-coloured needles, $C^{12}H^8Ca''(NO^2)^2O^2.H^2O$, or plates, $C^{12}H^8Ca''(NO^2)^2O^2.4H^2O$, which turn red when dehydrated. (Fritzsche.)

*Magnesium-salt.*—Magnesia boiled with nitrophenic acid forms a red solution which deposits needle-shaped crystals. Nitrophenic acid boiled with carbonate of magnesium expels only a portion of the carbonic acid. (Fritzsche.)

The soluble nitrophenates form orange-red precipitates with *acetate of lead* and *mercuric chloride* (Hofmann). The precipitates formed in solutions of nitrophenates by *zinc, copper*, and *lead-salts* quickly decompose, with separation of nitrophenic acid. (Fritzsche.)

*Silver-salt*, $C^6H^4Ag(NO^2)O$.—Orange-red precipitate, gelatinous and difficult to wash (Hofmann). Nitrate of silver added to a concentrated solution of a nitrophenate forms a deep orange-red precipitate which at first consists of microscopic needles, but in contact with the liquid soon changes to a powder consisting of thick crystals. A dilute solution of silver-nitrate mixed with a solution of nitrophenic acid in a slight excess of ammonia, deposits at first long needles of a deep red colour, between which orange-coloured crystals gradually form, and ultimately the entire deposit changes to a mass of granular crystals. The salt is anhydrous in both forms. (Fritzsche).

*Ethylic nitrophenate* or *Nitrophenetol*, $C^6H^4(C^2H^5)(NO^2)O$, is prepared by decomposing the silver-salt with ethylic iodide, exhausting with ether, evaporating the ethereal extract, and distilling the residual brown oily liquid. It then passes over as a nearly inodorous wine-yellow liquid, insoluble in water, easily soluble in alcohol and ether, slowly decomposed by boiling with potash (Fritzsche). The same compound appears to be formed, together with ethylic dinitrophenate or dinitrophenetol (p. 399), when ethylic phenate is treated with fuming nitric acid. (Cahours.)

**Isonitrophenic acid.** $C^6H^5(NO^2)O$. (Fritzsche, Petersh. Acad. Bull. xvii. 145; J. pr. Chem. lxxv. 257; Jahresh. 1858, p. 407.)—This acid, which has the same composition as nitrophenic acid, but differs from it in its properties and in the constitution of its salts, is produced, simultaneously with nitrophenic acid, in the first stage of the action of nitric acid on aqueous phenol. It is found in the residue left after the nitrophenic acid has been distilled off; but in order to obtain it from this residue, it is important to ensure the absence of dinitrophenic acid, and therefore not to use an excess of nitric acid. Fritzsche therefore dissolves 4 pts. of phenol in 100 pts. of hot water, adds 5 pts. fuming nitric acid of specific gravity 1·51, previously diluted with 20 pts. of water, and distils off about a third or half of the mixture. The distillate contains a large quantity of nitrophenic acid; the residue is free from dinitrophenic acid, and consists of a dark brown resinous body, which for the most part adheres closely to the sides of the retort, and a yellow liquid which separates in oily drops on cooling. This liquid, together with the solution obtained by boiling the resinous mass with water, is filtered hot, and immediately supersaturated with caustic soda, in which isonitrophenate of sodium is insoluble. This sodium-salt, which separates on cooling as a yellow crystalline powder, is separated from the liquid by filtration through pounded glass, washed with a little soda-ley, and crystallised from the smallest possible quantity of boiling water, from which it separates on cooling in prismatic or tabular crystals. To isolate the isonitrophenic acid, a solution of the sodium-salt, saturated at mean temperature, is mixed with hydrochloric acid at the temperature of about 40°, till the previously yellow liquid has become colourless: the acid then separates on cooling, first in oily drops, afterwards in slender needles. To purify it by recrystallisation, it must be dissolved in water not hotter than 40°, since at higher temperatures a portion of the acid separates in the liquid state, and usually with a yellowish-red colour, which it retains even after solidifying.

*Properties.*—Isonitrophenic acid crystallises from its pure aqueous solution in slender colourless needles; but by spontaneous evaporation of an ethereal solution, it may be obtained in larger crystals which assume a yellowish-red colour on exposure to light and air. These two forms are distinguished by Fritzsche as the colourless and the coloured modification. The acid is not, however, dimorphous; for, according to Kokscharow, both forms are monoclinic, and have their principal axis clinodiagonal and orthodiagonal in the same ratio, viz. as 1·0338 : 1 : 1·5094, and the two former axes inclined at an angle of 76° 37′. The crystals of the coloured modification exhibit the combination oP . + P . ∞P½ . ∞P∞, while the needle-shaped crystals of the colourless modification exhibit at the ends only the face ½P.

Isonitrophenic acid is inodorous, has a sweetish taste, with burning after-taste. It dissolves very easily in *alcohol;* the solution becomes milky on addition of water, and the acid which gradually collects together, remains liquid for days, if only a small quantity of water has been added. In the dry state it melts at about 110°; under water between 48° and 50°. At a stronger heat, it boils and passes over for the most part undecomposed; it volatilises perceptibly, however, at lower temperatures, even below its melting point, also with aqueous vapour when boiled with water. It is scarcely attacked by strong *sulphuric acid*, even after prolonged boiling. When it is treated with *iron filings* and dilute *acetic acid*, a violent action takes place, and a dark brown sparingly soluble iron-salt is formed, containing a peculiar acid not yet examined.

*Isonitrophenates.*—Isonitrophenic acid is a weak acid; it expels carbonic acid from the carbonates of the alkali-metals, and from magnesia alba; but scarcely attacks the carbonates of the other earth-metals, even at the boiling heat. It forms but one ethyl-compound, and is therefore probably monobasic; nevertheless, it forms two classes of salts, namely *neutral salts*, $C^6H^4M'NO^3$ or $C^{12}H^8M''N^2O^6$, which are mostly yellow or brownish-yellow in the hydrated, and brick-red in the anhydrous state; and *acid salts*, $C^6H^4MNO^3.C^6H^5NO^3$ or $C^{12}H^8M''N^2O^6.C^{12}H^{10}N^2O^6$, from which the second atom of acid may be removed by ether.

The *neutral ammonium-salt* (obtained from a solution of the acid in excess of warm aqueous ammonia) and the *acid salt* (by cautiously adding acetic acid to a cold saturated solution of the preceding) crystallise in yellow needles; both salts melt when heated, and give off their ammonia.—*Potassium-salts.* The acid dissolves easily in dilute potash-ley; and on adding excess of potash to this solution, the *neutral salt* $C^6H^4KNO^3.2H^2O$ separates as a golden-yellow microscopically crystalline precipitate, which, when recrystallised from a small quantity of hot water, forms confused crusts of crystals containing $C^6H^4KNO^3.2H^2O$; they give off their water at 130°, but recover it on exposure to the air. From a cold concentrated solution of this salt mixed with a little acetic acid, or from a solution of the neutral salt and the free acid in equivalent proportions, the *acid salt*, $C^6H^4KNO^3.C^6H^5NO^3$, separates in prismatic crystals which appear also to contain 2 at. water, but give off acid as well as water when heated.—*Sodium-salts.* A solution of the *neutral sodium-salt* prepared as above described (p. 395) yields at ordinary temperatures yellow-brown crystals which contain $C^6H^4NaNO^3.4H^2O$, give off half their water on exposure to the air, becoming opaque and yellow, and the remainder at 110°; the anhydrous salt, which has a brick-red colour, takes up 2 at. water, and becomes yellow again on exposure to the air. On adding acetic acid by drops to a cold saturated solution of the neutral sodium-salt, the *acid salt* is soon deposited in prismatic crystals, which, when recrystallised from water, yield slender orange-red prisms containing $C^6H^4NaNO^3.C^6H^5NaO^3.2H^2O$.

*Barium-salts.* The *neutral salt*, $C^{12}H^8Ba''N^2O^6.8H^2O$, crystallises from a mixture of the neutral sodium-salt and chloride of barium, in brown-yellow monoclinic prisms with basal end-faces; it slowly gives off half its water when exposed to the air, and becomes anhydrous at 120°.—The *acid salt*, $C^{12}H^8Ba''N^2O^6.C^{12}H^{10}N^2O^6.4H^2O$, separates in distinct crystals from a mixture of the neutral salt and the free acid in equivalent proportions.—In like manner are obtained the *neutral strontium-salt*, $C^{12}H^8Sr''N^2O^6.7H^2O$, in yellow needles; the *acid strontium-salt* in light yellow prisms;—also the *neutral calcium-salt*, $C^{12}H^8Ca''N^2O^6.4H^2O$, in yellow needles, and the *acid calcium-salt* $C^{12}H^8Ca''N^2O^6.C^{12}H^{10}N^2O^6.8H^2O$, which separates from a hot solution on cooling in short flat prisms.

The *magnesium-salt*, $C^{12}H^8Mg''N^2O^6.8H^2O$, crystallises from a mixture of the hot solutions of the neutral sodium-salt and sulphate of magnesium, or from the solution obtained by boiling the aqueous acid with excess of magnesia alba, in flat prisms or tablets.—An acid magnesium-salt does not appear to exist.

Solutions of *copper* and *zinc-salts*, added to soluble isonitrophenates, throw down

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precipitates consisting of basic salts, while free isonitrophenic acid remains in solution.

*Lead-salts.* The *neutral salt* has not been obtained.—By dropping a solution of the sodium-salt into a boiling solution of neutral lead-acetate, the salt $3C^{12}H^{8}Pb''N^{2}O^{6}.2Pb''O$, is obtained as an orange-coloured precipitate, flocculent at first but soon changing to a granular mass of microscopic six-sided tablets.—An *acid lead-salt* separates on cooling from a solution of isonitrophenic acid in hot aqueous neutral acetate of lead, in light yellow needles, which after recrystallisation contain $4C^{12}H^{8}Pb''N^{2}O^{6}.C^{12}H^{10}N^{2}O^{6}$.

*Silver-salts.*—The precipitates formed on mixing solutions of alkaline isonitrophenates and silver-nitrate, differ in composition according to the constitution of the soluble isonitrophenate used, the concentration, temperature, and proportions of the mixed solutions, and the manner in which they are brought together. The *neutral silver-salt* containing when air-dried, $C^{6}H^{4}AgNO^{3}.H^{2}O$, is obtained, on dropping a cold solution of neutral isophenate of sodium or ammonium into solution of silver-nitrate, as a bulky scarlet precipitate, which soon changes under the liquid to a mass of microscopic prisms of a deep orange-yellow colour. If, on the contrary, nitrate of silver be added, with stirring, to a cold aqueous solution of neutral isonitrophenate of ammonium, the liquid becomes milky, a red precipitate is formed, and afterwards a permanent light-yellow precipitate consisting of a double isophenate of silver and ammonium. When a mixture of the hot solutions of a neutral alkaline isonitrophenate and silver-nitrate is left to cool, especially if the latter is in excess, an *acid silver-salt*, $5C^{6}H^{4}AgNO^{3}.C^{6}H^{5}NO^{3}$, separates in purple needles, which if left in the liquid, ultimately change into the neutral-salt. A mixture of the warm solution of the acid sodium-salt with excess of a concentrated solution of silver-nitrate, also yields crystals of the purple salt just mentioned; but the last portions redissolved in the liquid after complete cooling, and in their place there are formed yellowish-green laminæ of the normal acid salt $C^{6}H^{4}Ag(NO^{3}).C^{6}H^{5}NO^{3}.H^{2}O$, which quickly turn scarlet on exposure to the air. On dissolving either of the preceding silver-salts in ammonia, an *isonitrophenate of argentammonium* is formed. A double isonitrophenate of ammonium and argentammonium has also been obtained in rather large crystals.

*Ethylic Isonitrophenate* or *Isonitrophenetol*, $C^{6}H^{4}(C^{2}H^{5})(NO^{2})O$, is obtained by decomposing the neutral silver-salt with ethylic iodide, distilling off the excess of the latter and exhausting the residue with ether. It crystallises in colourless prisms, easily soluble in ether, less soluble in alcohol, insoluble in water; has a peculiar aromatic odour; melts at 57°—58° to an oily liquid which solidifies in a crystalline mass; begins to boil at a stronger heat, and may be distilled for the most part without decomposition. (Fritzsche.)

**Nitro-dichlorophenic acid.** $C^{6}H^{3}Cl^{2}(NO^{2})O$.—Obtained by treating rectified coal-tar naphtha, first with chlorine, then with nitric acid. The product mixed with water is neutralised with ammonia, and boiled; the filtered solution is neutralised with ammonia, and the nitro-dichlorophenic acid which separates on cooling is purified by recrystallisation from alcohol. It is yellow, soluble in *water*, moderately soluble in boiling *alcohol* and in *ether*, and crystallises in beautiful monoclinic prisms having the angle $\infty P : \infty P = 88^{\circ}$; $\infty P : oP = 108^{\circ}\ 20'$ to $108^{\circ}\ 30'$. When quickly heated in a close vessel, it decomposes with ignition.

The *ammonium-salt* crystallises in beautiful orange-red needles which when cautiously heated partly sublime without decomposition. The *potassium-salt*, $C^{6}H^{2}KCl^{2}(NO^{2})O$, crystallises in very brilliant laminæ, which exhibit by reflection two very different colours, appearing of a fine crimson in one direction, and pure yellow in another. The other salts resemble the trinitrophenates or picrates. (Laurent and Delbos, Ann. Ch. Phys. [3] xix. 380.)

**Nitro-di-iodophenic acid.** $C^{6}H^{3}I^{2}(NO^{2})O$.—Formed by treating hot nitro-salicylic acid with iodine and adding potash. Its properties have not been examined. (Piria, Compt. rend. xvi. 187.)

**Dinitrophenic acid.** $C^{6}H^{4}N^{2}O^{5} = C^{6}H^{4}(NO^{2})^{2}O$. *Nitrophenesic acid.* (Laurent, Ann. Ch. Phys. [3] iii. 212.)—This acid is produced by the comparatively moderate action of nitric acid on phenol (Laurent); also by boiling dinitranisol (methylic dinitrophenate, i. 305) with alcoholic potash. (Cahours, Ann. Ch. Phys. [3] xxv. 22.)

*Preparation.*—12 pts. of commercial nitric acid are added by separate portions in a large porcelain basin to 1 pt. of that portion of coal-tar naphtha which boils between 160° and 190°, a fresh portion being added as soon as the violent intumescence caused by the preceding has subsided, in which case the mixture becomes hot enough to render external heating unnecessary. The resulting thick red-brown mass is freed by water from the greater part of the nitric acid; the residue boiled with very dilute ammonia; the solution while hot rapidly filtered from a brown resinous mass which serves for the preparation of picric acid; the brown crystalline substance which separates within 24 hours from the dark brown filtrate, is collected (an additional quantity of the brown resinous mass serving for the preparation of picric acid may be precipitated from the mother-liquor by acids); the crystalline substance is dissolved in boiling water; the delicate needles of dinitrophenate of ammonium which form on cooling, are purified by four recrystallisations (the matter precipitated from the mother-liquors by nitric acid serves also for the preparation of picric acid), washed with cold water, and dissolved in a very large quantity of boiling water; the solution is filtered as quickly as possible from any of the brown mass that may be precipitated; the mother-liquor is decanted from the acid which crystallises on cooling, boiled with fresh ammonia, again mixed with nitric acid, &c., and finally the acid thus obtained in fork-like tufts, is dissolved in boiling alcohol to purify it from a small quantity of oil: it then crystallises free from oil on cooling. (Laurent.)

*Properties.*—Dinitrophenic acid forms pale brown-yellow prisms belonging to the trimetric system, and exhibiting the combination $\infty P . \infty \breve{P}\infty . \breve{P}\infty$ with $\breve{P}$ very subordinate. Angle $\infty P : \infty P = 130°$; $\infty P : \infty \breve{P}\infty = 115°$; $\infty \breve{P}\infty : \breve{P}\infty = 127°$. Ratio of principal to secondary axes = 1·00 : 0·619 : 1·327. It melts at 104°, and solidifies in a radiated mass on cooling; may be distilled in small quantities without decomposition. It is inodorous; tasteless at first, afterwards very bitter; colours the cuticle, horn, and other animal tissues, deep yellow (Laurent). It is insoluble in cold, sparingly soluble in hot *water;* easily soluble in *alcohol* and *ether*, the latter when hot taking up rather more than a fourth of its weight of the acid.

*Decompositions.*—1. The acid detonates when suddenly heated in a tube, or slightly when heated in the air, with red flame and black smoke, leaving a residue of charcoal. —2. When heated with *bromine*, it is converted into dinitrobromophenic acid. *Chlorine* appears not to act upon it.—3. By boiling *nitric acid* it is quickly converted into picric acid (Laurent).—4. When heated with *chlorate of potassium* and *hydrochloric acid*, it is very easily converted into perchloroquinone (Hofmann, Ann. Pharm. lii. 62).—5. It dissolves in warm *fuming oil of vitriol*, and then decomposes, with rapid evolution of gas, turning brown and thickening at the same time.—6. It dissolves gradually in *dilute sulphuric acid*, in presence of *zinc*, forming a rose-coloured liquid, which is turned green by excess of ammonia, without precipitation.—7. When digested with dilute *sulphuric acid* and *baryta*, out of contact of air, it forms a blood-red liquid (Laurent).—8. When gently heated with aqueous *sulphide of ammonium*, it forms a nearly black liquid which on cooling deposits needles of nitrophenamic acid:

$$\underset{\substack{\text{Dinitrophenic}\\ \text{acid.}}}{2C^6H^4(NO^2)^2O} \quad + \quad 3H^2S \quad = \quad \underset{\substack{\text{Nitrophenamic}\\ \text{acid.}}}{C^{12}H^6(NO^2)^2N^2O^2} \quad + \quad 4H^2O \quad + \quad S^3.$$

9. *Chloride of benzoyl* attacks dinitrophenic acid when heated with it, giving off hydrochloric acid and forming dinitrophenylic benzoate or dinitrobenzophenide (i. 544).—10. With *pentachloride of phosphorus* the acid gives off hydrochloric acid and phosphoric oxychloride and forms dinitrophenylic chloride.

The metallic dinitrophenates are obtained, sometimes by saturating the acid with the pure base or its carbonate, sometimes by double decomposition. They are yellow or roseate and crystallisable. They all dissolve in water, and in this form impart a strong yellow colour to animal tissues. Heated somewhat above the melting point of lead, they detonate very slightly, with emission of light. Sulphuric, hydrochloric and nitric acid separate the acid from them.

The *ammonium-salt* crystallises from boiling water in long thin yellow needles having a silky lustre. By sublimation, yellow shining laminæ are obtained. Very sparingly soluble in water, still less in alcohol.

The *potassium-salt*, $2C^6H^3K(NO^2)^2O.H^2O$, forms yellow, shining, six-sided needles, with angles of 115°. They redden when heated, without alteration of weight; decompose and become opaque below 100°; give off 3·90 per cent. water in vacuo at 100°; melt at a stronger heat, and then detonate. They dissolve sparingly in cold water, very sparingly in cold alcohol, more easily in hot alcohol. The *sodium-salt* forms yellow, silky needles, which dissolve pretty easily in water.

The *barium-salt*, $C^{12}H^6Ba''(NO^2)^4O^2.5H^2O$ crystallises in thick, roseate, six-sided oblique prisms and needles, with two angles of the lateral edges of 89°, and four of 135° 30′. In vacuo, at ordinary temperatures, they give off 6·5 per cent. (2 at.) and at 100° altogether, 15·42 per cent. (5 at.) water.

The ammonium-salt mixed with *chloride of strontium*, the solutions being hot and concentrated, soon forms silky needles; with *chloride of calcium*, granules consisting of needles; with *alum*, needles. It does not precipitate the salts of *magnesium, manganese, cadmium, cobalt, nickel*, or *copper*, or *mercuric salts.*

*Dinitrophenate of Cobalt* forms brown-yellow, right rectangular prisms, with dihedral summits. Its brown aqueous solution forms with ammonia a yellow precipitate which melts and detonates when heated. The *copper-salt* crystallises in yellow silky needles, whose yellow solution forms with ammonia, yellow needles sparingly soluble in ammonia or in water.

*Lead-salts.*—The neutral salt has not been obtained. A *basic lead-salt*, $2C^{12}H^6Pb''(NO^2)^4O^2.Pb''O$, is formed on pouring a boiling alcoholic solution of the acid into a moderately concentrated boiling alcoholic solution of neutral acetate of lead, and crystallises on cooling in spherical groups of microscopic needles having a fine yellow colour. Another *basic salt*, $C^{12}H^6Pb''(NO^2)^4O^2.4H^2O$, is obtained on pouring dinitrophenate of ammonium into a boiling dilute solution of neutral lead-acetate. It is one of the most powerfully detonating of all salts. The ammonium-salt forms with solution of nitrate of silver a reddish-yellow precipitate, or in case of greater dilution, after a while, needles which dissolve in a large quantity of water or alcohol. (Laurent.)

*Dinitrophenic ethers.*—1. *Methylic dinitrophenate* or *Dinitranisol*, $C^7H^6N^2O^5 = C^6H^3(CH^3)(NO^2)^2O$, has been already described; also the base *Methyl-nitrophenidine* or *Nitranisidine*, $C^7H^8(NO^2)NO$, formed from it by the action of sulphide of ammonium.

*Ethylic Dinitrophenate, Dinitrophenetol* or *Dinitrosalithol*, $C^8H^8N^2O^5 = C^6H^3(C^2H^5)(NO^2)^2O$, is obtained by treating ethylic phenate (p. 391) with an equal volume of fuming nitric acid, added by small portions, and boiling the liquid for a few minutes till it becomes clear, and then adding water. Dinitrophenetol is thereby precipitated as an oil which ultimately solidifies, and may be crystallised from boiling alcohol. It crystallises in yellow needles very much like dinitranisol. When cautiously heated, it sublimes without residue; but if quickly heated, it decomposes with ignition, leaving an abundant deposit of charcoal. Sulphide of ammonium converts it into ethyl-nitrophenidine, $C^8H^{10}(NO^2)NO$.

**Dinitrobromophenic acid,** $C^6H^3BrN^2O^5 = C^6H^3Br(NO^2)^2O$. *Nitrobromophenesic acid.* (Laurent, *Rev. scient.* vi. 65.)—This acid is produced by dissolving dinitrophenic acid in heated bromine, washing the crystals which separate on cooling with a small quantity of alcohol, dissolving them in boiling ether, and leaving the solution to crystallise in a beaker covered with paper. It is sulphur-yellow, transparent; crystallises from ether in shining monoclinic prisms having the angle $\infty P : \infty P = 106° 30'$; $0P : \infty P = 98° 30'$.—From boiling water or alcohol, it separates in needles. It melts at about 110°, and solidfies on cooling into a laminar fibrous mass. When strongly heated, it distils partly undecomposed and leaves a small quantity of charcoal. Permanent in the air, inodorous, colours the skin yellow, like picric acid. It dissolves very sparingly in boiling *water*, and separates almost completely on cooling; with moderate facility in boiling *alcohol*, more easily in *ether*. It dissolves also in warm oil of vitriol and crystallises therefrom in fern-like tufts.

*Decompositions.*—1. The acid is not decomposed by *chlorine* in the cold and but slightly when heated.—2. By boiling *nitric acid* it is converted into picric acid.—3. Its solution in warm *oil of vitriol* decomposes when heated.—4. Its aqueous solution forms with *ferrous sulphate* and *lime*, a blood-red liquid, with precipitation of ferric oxide.

The dinitrobromophenates are yellow, orange-coloured or red; crystallise well; resemble the picrates; detonate for the most part, like those salts, when heated, but less strongly, and in a closed space with emission of light; they dissolve for the most part in water, from which solution, sulphuric, hydrochloric or nitric acid separates the dinitrobromophenic acid.

The *ammonium-salt* forms yellow eight-sided needles derived from a rhombic prism. In vacuo at 100° they give off 8·57 per cent. water, and 1·86 per cent. more at a heat nearly sufficient to volatilise them, and then sublime, for the most part undecomposed, in yellow, shining right rhombic prisms, with lateral edges of 45° and 135°.—The *potassium-salt* forms yellow, silky needles, sparingly soluble in water and alcohol.

The *barium-salt*, $C^{12}H^4Br^2Ba''(NO^2)^4O^2.4H^2O$, forms dark yellow needles, which dissolve very readily in water, give off in vacuo at ordinary temperatures, 7·5 per cent. (3 at.) water, assuming a scarlet colour, and at 100°, 9·42 per cent. (4 at.) in all.

The *calcium-salt* forms long yellow laminæ, which are oblique rectangular prisms. They turn about on recently dried paper or in vacuo, giving off water and assuming a scarlet colour. The ammonium-salt does not form any precipitate with *chloride of strontium, magnesium* or *manganese*.

*Lead-salt.*—When a boiling dilute solution of the ammonium-salt is poured into a boiling dilute solution of neutral acetate of lead, there is immediately formed an orange-yellow precipitate of a basic salt containg 37 per cent. lead-oxide; and the liquid decanted therefrom after some seconds, forms pale yellow silky needles of the *diplumbic salt* $C^{12}H^4Br^2Pb''(NO^2)^4O^2.Pb''H^2O^2$, which give off 3·3 per cent. (2 at.) water in vacuo at 100°, and contain 44·0 per cent. lead-oxide.—In solutions not too dilute, the ammonium-salt forms with lead-salts, a heavy, yellow, crystalline precipitate.

The ammonium-salt forms with the salts of *cadmium, cobalt, nickel* and *copper*, on addition of ammonia, a precipitate which consists of needle-shaped particles, scarcely soluble in ammonia.

With *nitrate of silver*, the ammonium-salt forms a yellow translucent precipitate; from very dilute solutions, the silver-salt is deposited in extremely fine filaments.

**Dinitrochlorophenic acid.** $C^6H^3ClN^2O^5 = C^6H^3Cl(NO^2)^2O$ (P. Griess, Ann. Ch. Pharm. cix. 286.)—Prepared by passing a moderately strong stream of chlorine into about a pound of phenol, kept at a moderate heat, and adding the product by small portions to nitric acid of ordinary strength, in a capacious porcelain dish. The action begins in the cold, and is attended with the evolution of red, intensely irritating vapours, smelling like chloropicrin, but towards the end a gentle heat must be applied till red vapours are no longer given off. The resulting red oily mass, consisting chiefly of dinitrochlorophenic acid, is washed with water to free it from excess of nitric acid, and from oxalic acid formed in the reaction, and then treated with aqueous ammonia; the crystalline magma thus produced (consisting chiefly of dinitrochlorophenate of ammonium) is dissolved in hot water, and quickly filtered; the yellow needles of the ammonium-salt, which separate as the filtrate cools, are once recrystallised,* and the solution of the purified salt in boiling water is decomposed by dilute nitric acid.

Dinitrochlorophenic acid thus prepared crystallises in light yellow anhydrous laminæ. It is but slightly soluble in hot water, and separates almost completely in yellow laminæ on cooling. It dissolves more readily in *alcohol* and *ether*, abundantly also in hot *hydrochloric, nitric*, and *sulphuric acids*, separating from these solutions on cooling, especially on addition of water, in nearly colourless laminæ. It melts at 103°, solidifying again to a radio-crystalline mass at 95°, and sublimes without alteration. In powder or in vapour it excites violent coughing and sneezing; it tastes intensely bitter like picric acid, and colours the skin yellow.

The acid or its ammonium-salt, digested at a gentle heat with aqueous *sulphide of ammonium*, is converted, with deposition of sulphur, into amidonitrochlorophenic acid, $C^6H^3(NH^2)(NO^2)ClO$.

The dinitrochlorophenates crystallise well; they are all sparingly soluble in water, and are deposited from hot aqueous solution on cooling in reddish or yellow crystals: they detonate when heated. The *ammonium-salt*, $C^6H^2(NH^4)Cl(NO^2)^2O$, crystallises in shining yellow needles, green by reflected light, and begins to sublime at 100°. The *potassium-salt* forms shining orange-yellow needles. The *barium-salt*, obtained by saturating the aqueous acid with carbonate of barium, crystallises in delicate yellow needles, which turn red in rarefied air over oil of vitriol, and then contain $C^{12}H^2Ba''Cl^2(NO^2)^4O^2.H^2O$: the red crystals recover their yellow colour on exposure to the air, and the salt becomes anhydrous at 110°. The *silver-salt* separates on adding nitrate of silver to a concentrated solution of the ammonium-salt; when recrystallised it forms crimson laminæ with green iridescence, which appear under the microscope as oblique rhombic prisms. With *copper* the acid appears to form several salts: a solution of recently-prepared cupric oxide in the aqueous acid, yields on evaporation yellow needles easily soluble in water.

**Trinitrophenic** or **Picric acid.** $C^6H^3N^3O^7 = C^6H^2(NO^2)^3O$. *Trinitrocarbolic acid. Carbazotic acid. Nitropicric acid. Artificial Indigo-bitter. Kohlenstickstoffsäure. Jaune amer de Welter.*—This acid was observed by Hausmann in 1788, and afterwards examined, with regard to its composition, chiefly by Liebig (Pogg. Ann. xiii. 191; xiv. 466; Ann. Ch. Pharm. ix. 80; xxxix. 350), Dumas (Ann. Ch. Phys. liii. 178 [3] ii. 228), and Laurent (*ibid.* [3] iii. 221).

It is produced: 1. By the action of heated nitric acid on phenic, tribromophenic, and dinitrophenic acid, also on saligenin, salicylous acid, salicin, salicylic acid, nitrosalicylic acid, phlorizin, extract of willow-bark, indigo, coumarin, aloes, benzoin, the resin of *xanthorhæa hastilis*, resin of Peru balsam, and silk.—2. By boiling trinitranisol with potash-ley. (Cahours.)

*Preparation.*—1. *From Phenol.*—The brown resinous masses precipitated during the preparation of dinitrophenic acid (p. 397), are united with the mass obtained by precipitating with nitric acid the mother-liquors of dinitrophenate of ammonium obtained in the same process; the united mass is heated to the boiling point in a basin with commercial nitric acid; the acid liquid decanted after cooling; the residue washed with a small quantity of cold water, and boiled with very dilute ammonia; the filtrate repeatedly evaporated to the crystallising point; the resulting picrate of ammonium purified by crystallisation from boiling alcohol; and the beautiful needles of this salt treated with nitric acid to separate the picric acid, the quantity of which, thus obtained,

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* The mother-liquor retains in solution the ammonium-salt of another acid formed during the above reaction, and if mixed while still hot with hydrochloric acid, deposits this acid as a viscid oil, which ultimately solidifies. It melts easily, and is converted by sulphide of ammonium into an amido-acid. Nitrodichlorophenic acid (p. 397) does not appear to be formed in this reaction.

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is greater as the quantity of dinitrophenic acid was less. The impure dinitrophenic acid may also be converted into picric acid by boiling it with nitric acid, and recrystallising from alcohol the portion which separates out (Laurent). Picric acid may, however, be more advantageously prepared from pure crystallised phenol, which is now manufactured in large quantities from coal-tar; this is in fact the mode of preparation now most generally adopted. 100 pts. of crystallised phenol, treated with nitric acid, yield, according to Perra (Dingl. pol. J. clxv. 386), from 90 to 100 pts. of picric acid.

2. *From Salicin.*—This substance, treated with nitric acid, yields remarkably pure picric acid; *phlorizin* yields much less picric than phloretic acid. (Marchand.)

3. *From Indigo.*—12 to 13 pts. of nitric acid of specific gravity 1·43 are heated nearly to the boiling point in a capacious glass flask; 1 pt. of the best East Indian indigo in coarse powder, is added in small portions, each addition being made as soon as the last portion has disappeared; the red-brown liquid is concentrated by boiling till it becomes thickish and lighter in colour; 3 pts. more nitric acid are added in case the liquid still gives off nitrous acid, and the boiling is repeated; the mother-liquor is decanted from the hard, yellow, translucent crystals which form on cooling; these crystals are washed with cold water and dissolved in a sufficient quantity of boiling water; the oily drops of artificial tannin which then rise to the surface are removed with filtering paper; the solution is filtered and left to cool; the yellow shining laminæ of picric acid which separate are removed from the mother-liquor, again dissolved in boiling water, and neutralised with carbonate of potassium; the potassium-salt which separates on cooling is purified by repeated crystallisation, then dissolved in boiling water; and the liquid is mixed with sulphuric, hydrochloric, or nitric acid, whereupon the picric acid crystallises out on cooling. An additional quantity of the potassium-salt, requiring, however, further purification, may be obtained from the first mother-liquor by precipitating therefrom a large quantity of brown matter by addition of water, then dissolving it in boiling water, neutralising with carbonate of potassium, and cooling. Four parts of indigo should yield 1 pt. of picric acid. Sometimes the solution of indigo in nitric acid does not yield any crystals; it must then be evaporated down, mixed with water, and the acid separated from the brown precipitate as above. The liquid above the precipitate likewise yields picric acid, when evaporated, boiled with nitric acid, neutralised with potash, &c. (Liebig). Altogether, however, the preparation of picric acid from indigo is not to be recommended.

4. *From the yellow resin of Xanthorrhœa hastilis.*—The resin is dissolved in the requisite quantity of strong nitric acid, whereupon red vapours are evolved, with violent frothing, and a dark-red solution is formed which becomes deep yellow after boiling. This solution is evaporated over the water-bath; the remaining yellow crystalline mass, which, together with picric acid, contains small quantities of oxalic and nitrobenzoic acids, is neutralised with potash; and the picrate of potassium is purified by two crystallisations, and then treated with hydrochloric acid, which separates the picric acid, to be further purified by two crystallisations, and amounting to 50 per cent. of the resin used (Stenhouse). This is one of the best modes of preparation (see Carey Lea, Sill. Am. J. [2] xxvi. 279; Jahresb. 1858, p. 414).

5. *From Benzoin.*—1 pt. of benzoin (from which the benzoic acid may be previously extracted by alkalis) is gently heated with 8 pts. of commercial nitric acid; the mixture distilled, with four times repeated cohobation, after the effervescence has ceased; and the liquid, after decantation from the resin, mixed with four times its bulk of water, filtered from the precipitated yellow powder, and neutralised while hot with carbonate of potassium: it then yields crystals of picrate of potassium on cooling. (E. Kopp, Ann. Chim. Phys. [3] xiii. 233.)

6. *From Silk.*—1. When 1 pt. of silk is distilled, with frequent cohobation, with 6 pts. of nitric acid, a solution is obtained which, by evaporation and cooling, yields crystals of picric and oxalic acids (Welter).—2. Liebig uses 12 pts. of nitric acid; neutralises the residue in the retort with carbonate of potassium; purifies the crystals of potassic picrate by recrystallisation; and precipitates the acid from their solution by nitric acid. The product from silk is however much smaller than that which is obtained from indigo.

7. *From Aloes.*—1 pt. of aloes is heated with 8 pts. of strong nitric acid till violent action takes place; the fire is then removed; the mixture, after the gas-evolution has ceased, is introduced into a retort; the greater part of the acid liquid poured off; the residue distilled with 3 or 4 pts. of fresh nitric acid, which still causes a slow evolution of nitric oxide, till the greater part of the nitric acid is decomposed or volatilised; the residue diluted with water, which separates the chrysammic and aloetic acids still remaining undecomposed; and the yellow filtrate after being evaporated, to remove the greater part of the nitric acid, is neutralised with milk of lime: pure picric acid may then be precipitated from the filtrate by nitric acid.

8. *From Trinitranisol.*—Trinitranisol is boiled for a few minutes with moderately strong potash; water is added till all the resulting potassium salt is dissolved; the salt allowed to crystallise by cooling; and the acid separated therefrom by boiling dilute nitric acid: it then separates on cooling in yellow shining needles, and may be purified by washing with cold water, and crystallisation from boiling water.[*] (Cahours, Ann. Ch. Phys. [3] xxv. 26.)

*Purification.*—The conversion of crude picric acid into a potassium-salt affords a very convenient mode of purification on the small scale, as the salt is but very slightly soluble in cold, though readily soluble in boiling water. But in operating on a large scale, the filtration of this salt presents great difficulties, as the liquids, even when boiling and contained in heated funnels, have a great tendency to crystallise on the filters, which they then rapidly choke. Several manufacturers therefore prefer converting the crude acid into a sodium-salt, by saturating the boiling solution with sodic carbonate, taking care to avoid an excess, as that would dissolve the yellow resinous matter with which the acid is contaminated. The boiling liquors are filtered to separate this resin, and the filtrate is mixed with a further quantity of sodic carbonate. This causes the bulk of the sodic picrate to crystallise out, as the salt is nearly insoluble in solutions containing an excess of alkaline carbonate. The small quantity of picric acid still remaining in the mother-liquors may be precipitated by adding a potassium-salt.

The crystallised picrate of sodium thus obtained is then dissolved, and its boiling solution is decomposed by an excess of sulphuric acid. The picric acid thus separated, being nearly insoluble in the mother-liquors containing the acid sulphate of sodium, crystallises out almost entirely on cooling; and after draining, washing with a little cold water, and pressing, is almost chemically pure. (*Hofmann's Report*, p. 136.)

*Properties.*—Picric acid cystallises in light yellow, strongly shining laminæ (Liebig), in yellowish octahedrons, often very much truncated on two of their summits (Welter); yellowish-white needles and granules (Chevreul). The crystals belong to the trimetric system. Angle $\infty P : \infty P = 115° 30'$; $P : P = 108°$; $\breve{P} : \infty\bar{P}\infty = 125°$ (Laurent). The acid melts when slowly heated, forming a brownish-yellow oil, which solidifies in a crystalline mass on cooling. When slightly heated in contact with the air, it volatilises undecomposed; at a higher temperature, it boils and gives off a thick, yellow, suffocating, irritating, and intensely bitter vapour, and sublimes in small yellowish-white needles and scales, or passes over as a brown liquid which crystallises on cooling. It tastes very bitter and somewhat harsh and sour, and reddens litmus. The impure acid from indigo in doses of 1 to 10 grains, kills rabbits and dogs, with delirium and convulsions.

Picric acid dissolves in 160 pts. of *water* at 5°, in 86 pts. at 15°, in 81 pts. at 20°, in 77 pts. at 22·5°, in 73 pts. at 26°, and in 26 pts. at 77° (Marchand). The solution has a deeper colour than the solid acid, and imparts a strong yellow stain to the skin and other animal tissues.

Water containing only $\frac{1}{10000}$ of picric acid is distinctly yellow; with $\frac{1}{30000}$ of the acid the colour is still perceptible in a stratum an inch deep, and in larger masses to a still greater degree of dilution. (Carey Lea.)

Picric acid is likewise easily soluble in *alcohol* and in *ether*. It dissolves in warm concentrated *sulphuric acid*, and is precipitated therefrom by water unchanged, and according to Lea, in square laminæ belonging to the trimetric system. A cold saturated solution of picric acid mixed with 2 to 4 vol. of dilute sulphuric acid (1 vol. oil of vitriol to 1 vol. water) remains nearly or quite colourless, without separation of picric acid: with $\frac{1}{2}$ or $\frac{1}{3}$ vol. sulphuric acid, nearly all the picric acid is precipitated (Carey Lea). Strong *nitric acid* dissolves picric acid in large quantity.

*Decompositions.*—1. The acid when strongly *heated*, gives off acrid and very bitter vapours, which condense as a sublimate on cold bodies; when quickly heated in a retort, it decomposes with explosion, giving off nitrogen, nitric oxide, water, carbonic anhydride, hydrocyanic acid, and a combustible gas, and leaving a carbonaceous residue.—2. By *chlorine gas*, aqueous *chloride of lime*, or a mixture of *hydrochloric acid and chlorate of potassium*, it is resolved into chloropicrin and perchloroquinone (chloranil); also by hot *nitromuriatic acid*; by *bromine* and water, into bromopicrin and perbromoquinone. It is also converted into bromopicrin by distillation with *hypobromite of barium* (Stenhouse, Phil. Mag. [4] viii. 363).—3. When gently heated with a mixture of *peroxide of manganese and sulphuric acid* it gives of nitrous vapours.—4. Boiled with a strong solution of caustic *potash*, it gives off a large quantity of ammonia, and forms a brown solution from which alcohol extracts a yellow salt crystallising in needles. Picric acid is likewise altered by prolonged ebullition with *baryta-water*.

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[*] The acids obtained by this and the preceding process were at first regarded as isomeric, but not identical, with picric acid, the acid from aloes being called *chrysolepic acid* (Schunck), and that from trinitranisol, *picranisic acid* (Cahours); but later experiments have shown that both these acids are identical with picric acid, the difference formerly observed having been due to impurities.

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3. When picric acid is digested with a solution of *ferrous sulphate* and an excess of caustic baryta or lime, a red-brown mass is formed containing picramic acid (Wöhler's nitrohæmatic acid):

$$\underset{\text{Picric acid.}}{C^6H^3(NO^2)^3O} + 6FeO + H^2O = \underset{\text{Picramic acid.}}{C^6H^5N(NO^2)^2O} + 3Fe^2O^3.$$

Picric acid is also reduced to picramic acid by *ferrous chloride* and *acetate; cuprous chloride, nascent hydrogen*, and by the *sulphides of ammonium* and of the *fixed alkali-metals;* most readily by passing sulphydric acid gas through a saturated *alcoholic* solution of picric acid neutralised with ammonia. (Girard, Ann. Ch. Pharm. lxxxviii. 281.)

4. Picric acid treated with *tin* and *hydrochloric acid* is converted into a crystalline double salt of stannous chloride and hydrochlorate of picramine, $C^6H^9N^3$ (Roussin, Bull. Soc. Chim. 1861, p. 60;—Beilstein, Ann. Ch. Pharm. cxxx. 244):

$$C^6H^3(NO^2)^3O + Sn^{10} + 23HCl = C^6H^9N^3.3HCl.SnCl^2 + 9SnCl^2 + 7H^2O.$$

The same base is obtained as a hydriodate by the action of *iodide of phosphorus* on a saturated aqueous solution of picric acid (Lautemann, Ann. Ch. Pharm. cxxv. 1):

$$C^6H^3(NO^2)^3O + 23HI = C^6H^9N^3.3HI + I^{20} + 7H^2O.$$

5. Picric acid treated with *cyanide of potassium* in the state of hot concentrated aqueous solution assumes a deep blood-red colour and is converted into isopurpuric acid (Hlasiwetz; Beilstein, iii. 433):

$$C^6H^3(NO^2)^3O + 3CNH + H^2O = C^8H^5N^5O^6 + CO^2 + NH^3.$$

According to Carey Lea (Jahresb. 1858, p. 415) picric acid is converted into picramic acid by the action of cyanide of potassium; but this statement is contradicted by Hlasiwetz and Beilstein (Jahresb. 1859, p. 458).

6. *Pentachloride of phosphorus* acts violently on picric acid, forming chloride of trinitrophenyl or chloropicryl (Pisani, Compt. rend. xxxix. 852):

$$C^6H^3(NO^2)^3O + PCl^5 = C^6H^2(NO^2)^3Cl + PCl^3O + HCl.$$

7. *Chloride of benzoyl* heated with picric acid converts it into benzoate of trinitrophenyl or trinitrobenzophenide (i. 554).

8. A mixture of *alcohol*, *sulphuric acid* and *picric acid* appears to yield picrate of ethyl. (Mitscherlich.)

*Detection of Picric Acid.*—As reagents for the detection of picric acid, Carey Lea recommends an ammoniacal solution of cupric sulphate, a solution of sulphide of potassium mixed with excess of alkali, and of cyanide of potassium with ammonia. The first produces a greenish precipitate, the other two when heated with the aqueous acid become red, or in case of very great dilution, yellow.

*Uses of Picric acid.*—Picric acid is used for dyeing silk and wool, especially the former, of a yellow colour. Its colouring power is very considerable, and it exhibits a great affinity for azotised substances. The colour resists the action of light very well, but is somewhat affected by washing, especially with soap. Its stability is increased by mordanting the silk and wool with alum.

Cotton, hemp and flax do not exhibit any affinity for picric acid; this acid may therefore be employed for distinguishing silk and wool from cotton and flax. For this purpose the tissue is immersed in a hot solution of picric acid and then washed with water; the threads of silk and wool then assume a deep yellow colour, while those of cotton and flax remain perfectly colourless.

The isopurpurate of potassium produced by the action of cyanide of potassium on picric acid yields, when treated with sal-ammoniac, an ammonium-salt possessing the external characters of murexide (purpurate of ammonium, *q. v.*), and acting exactly like that compound when applied to dyeing.

The coloured compounds produced by the action of ferrous and stannous salts on picric acid have not yet been applied to any practical purpose.

PICRATES.—Picric acid is monobasic. The metallic picrates are mostly crystallisable, bitter, and of yellow colour. They explode when strongly heated, especially in close vessels. By precipitating solutions of heavy metallic salts with alkaline picrates, Carey Lea (Sill. Am. J. [2] xxxi. 78) has obtained compounds of metallic picrates with ammonia. The silver-salt contains $2NH^3.C^6H^2Ag(NO^2)^3O$; the copper and cobalt compounds are represented by the formula $4NH^3.C^{12}H^4M''(NO^2)^6O^2$; the zinc and cadmium compounds by the formula $3NH^3.C^{12}H^4M''(NO^2)^6O^2$.

***Picrate of Aluminium*** separates after some days from a mixture of the hot solutions of chloride of aluminium and picrate of ammonium, in stellate groups of crystals which are permanent in the air. (Carey Lea, Sill. Am. J. [2] xxvi. 279.)

***Picrate of Ammonium***, $C^6H^2(NH^4)(NO^2)^3O$, crystallises in yellow four-, six-

and eight-sided prisms, belonging to the trimetric system, and exhibiting the combination $\infty P \,.\, \infty \breve{P}\infty \,.\, \infty \bar{P}\infty \,.\, P$. Angle $\infty P : \infty P = 111° : \infty P : \infty \bar{P}\infty = 145°$; $P : P$ (terminal) $= 135°$; $P : P$ (basal) $= 115°$ (**Laurent**, Rev. Scient. ix. 26). It is moderately soluble in water, sparingly in alcohol.

*Picrate of Barium*, $C^{12}H^4Ba''(NO^2)^6O^2.5H^2O$, crystallises in monoclinic prisms of deep yellow colour (yellow with red terminal faces, according to Lea), very soluble in water, fusible and explosive. The crystals contain 11·16 per cent. water of crystallisation, the greater part of which is given off at 100°

*Picrate of Cadmium* separates from the solution of the carbonate in hot aqueous picric acid, in large rhombic prisms, isomorphous with the ferrous and manganous salts (*infra*), very soluble and efflorescent; the aqueous solution when boiled for some time deposits a brown powder. (**Lea.**)

*Picrate of Calcium* forms prisms more soluble than the barium- and strontium-salts.

*Picrates of Chromium.* *Chromous* acetate dissolves in aqueous picric acid, forming a brown liquid which dries up to an amorphous mass. Basic *chromic* carbonate dissolves in aqueous picric acid forming a greenish solution which also dries up to an amorphous mass; but by exactly precipitating a solution of violet chromic sulphate with picrate of barium, and leaving the filtrate to evaporate, small greenish needle-shaped crystals are obtained. (**Lea.**)

*Picrate of Cobalt*, $C^{12}H^4Co''(NO^2)^6O^2.5H^2O$, forms dark brown needles which melt and give off all their water of crystallisation (14·4 per cent.) between 100° and 110°. (**Marchand.**)

*Picrate of Copper*, $C^{12}H^4Cu''(NO^2)^6O^2.5H^2O$.—When carbonate of copper is dissolved in boiling aqueous picric acid, the solution evaporated to dryness, and the residue treated with boiling absolute alcohol, neutral cupric picrate dissolves, while a basic salt remains behind. The neutral salt forms small green shining needles, efflorescent and melting at 100° (**Marchand**). On adding an ammoniacal solution of cupric sulphate to an alkaline picrate, a copious greenish-yellow precipitate is formed, which is resolved by water into cupric oxide and picrate of ammonium. (**Lea.**)

*Picrate of Glucinum* separates in golden-yellow crusts on evaporating a solution of carbonate of glucinum in hot aqueous picric acid. (**Lea.**)

*Picrates of Iron.*—The *ferrous salt* forms greenish-yellow crystals, isomorphous with the manganous salt. The *ferric salt* is obtained in yellowish-red prisms and yellow needles by exactly precipitating a solution of picrate of barium with ferric sulphate, and leaving the filtrate to evaporate. Aqueous picric acid dissolves but a small quantity of ferric hydrate, even at the boiling heat. (**Lea.**)

*Picrates of Lead.*—The *neutral salt*, $C^{12}H^4Pb''(NO^2)^6O^2$, is obtained in the form of brown needles moderately soluble in water, during the cooling of a boiling, slightly acidulated mixture of an alkaline picrate and acetate of lead. (**E. Kopp**, Ann. Ch. Phys. [3] xiii. 233.)

*Basic salts.*—α. By precipitating a dilute and boiling solution of neutral lead-acetate with picrate of ammonium containing a large excess of ammonia, a deep yellow powder is obtained, composed of rectangular prisms and containing $C^{12}H^4Pb''(NO^2)^6O^2.4Pb''O$. —β. A mixture of picrate of ammonium and slightly acidulated acetate of lead yields on addition of ammonia, a light yellow precipitate, which when left at rest, changes to a mass of shining scales, soft to the touch like talc, and containing $C^{12}H^4Pb''(NO^2)^6O^2.2Pb''O.3H^2O$ (**Marchand**).—γ. A boiling mixture of picrate of ammonium and acetate of lead deposits, according to Laurent, small dark yellow rhomboïdal tables apparently containing $C^{12}H^4Pb''(NO^2)^6O^2.Pb''H^2O^2$.

A *picro-acetate of lead*, $C^{12}H^4Pb''(NO^2)^6O^2.C^4H^6Pb''O^4.4H^2O$ (**Marchand**), is deposited in light yellow, very brilliant rhomboïdal tablets, when a boiling mixture of potassic picrate and an excess of lead-acetate is left to cool. This compound gives off acetic acid when dried.

*Picrate of Magnesium* forms long flattened needles, of yellow colour, very soluble in water, nearly insoluble in boiling alcohol, and apparently containing 5 at. water of crystallisation. (**Marchand.**)

*Picrate of Manganese*, $C^{12}H^4Mn''(NO^2)^6O^2.8H^2O$ (**Marchand**).—A solution of manganous carbonate in hot aqueous picric acid crystallises by slow evaporation in large rhombic crystals exhibiting the combination $\infty \breve{P}\infty \,.\, \infty \bar{P}\infty \,.\, \infty P \,.\, oP$, and appearing pale yellow in the direction of the principal axis, reddish in every other direction (**Lea**). According to Marchand, the crystals quickly give off 3 at. water on exposure to the air and 4 at. more at 130°.

*Picrates of Mercury.*—The *mercuric salt* is deposited in small yellow prisms very slightly soluble in cold water, during the cooling of a boiling mixture of mercurous nitrate and picrate of potassium (Liebig). The *mercuric salt* separates from a solution of mercuric oxide in aqueous picric acid, in orange-coloured shining needles, which effloresce and turn yellow on exposure to the air. (Lea.)

*Picrate of Nickel*, $C^{12}H^4Ni''(NO^2)^6O^2.8H^2O$, is obtained by spontaneous evaporation of a solution of hydrate or carbonate of nickel in aqueous picric acid, in green, dichroic, efflorescent crystals, very soluble in alcohol. (Marchand.)

*Picrate of Potassium*, $C^6H^2K(NO^2)^3O$, is obtained by neutralising a hot aqueous solution of picric acid with potash, or, according to Liebig, in the state of greatest purity by digesting an aqueous solution of potassic chloride with mercurous picrate. It crystallises in yellow rhombic prisms, usually with a metallic reflex. Observed combination $\infty P . \infty \breve{P}\infty . \breve{P}\infty$. Angle $\infty P : \infty P = 110° 15' 30''$; $\breve{P}\infty : \breve{P}\infty$ in the brachydiagonal principal section $= 139° 25'$. Ratio of vertical to horizontal axes $= 1 : 2{\cdot}70456 : 1{\cdot}88469$ (Laurent, Rev. scient. x. 26). It is but slightly soluble in water, requiring for solution at least 260 pts. water at 15°, and 14 pts. of boiling water; insoluble in alcohol. Hence picric acid forms a precipitate in solutions of potassium-salts if not too dilute, especially on addition of alcohol. When heated, it assumes an orange colour, but becomes yellow again on cooling; when strongly heated, it decomposes with detonation.

*Picrate of Silver*, $C^6H^2Ag(NO^2)^3O$, forms fine yellow shining needles very soluble in water.

*Picrate of Sodium* forms slender shining yellow needles, soluble in 10 to 14 pts. of water at 15°, and detonating rather strongly at a high temperature. According to Lea, an alcoholic solution of picric acid forms a precipitate after a while, in alkaline solutions of sodium-salts, when not very dilute: hence picric acid cannot be depended upon as a test for distinguishing between potassium and sodium.

*Picrate of Strontium*, $C^{12}H^4Sr''(NO^2)^6O^2.5H^2O$, forms hard, shining, yellow crystals, moderately soluble in cold water, very slightly soluble in boiling absolute alcohol. It detonates when heated.

*Picrate of Zinc*, $C^{12}H^4Zn''(NO^2)^6O^2.7H^2O$? forms beautiful rhomboïdal prisms, efflorescent, very soluble in water and in alcohol. It gives off 8 per cent. water in dry air, at ordinary temperatures, and 14 per cent. (in all) at 140°.

PICRATES, ALCOHOLIC. PICRIC ETHERS.—The only known compound of this class is the picrate of ethyl, which is produced, according Mitscherlich, by boiling an alcoholic solution of picric acid containing a little sulphuric acid for several hours, then adding ammonia and water. The product crystallises in scales having a faint yellow colour, melts at 94°, and begins to boil and decompose at 300°. It is inodorous, but has a biting and bitter taste. It is sparingly soluble in cold, more soluble in hot alcohol (Mitscherlich, J. pr. Chem. xxii. 195). Erdmann (*ibid.* xxxvii. 413) was not able to prepare picric ether by the process just described.

PICRATES OF ORGANIC BASES. (See the several BASES.)

PICRATES OF HYDROCARBONS.—Crystalline compounds of picric acid with benzene, naphthalene, and other hydrocarbons, have been obtained by Fritzsche (J. pr. Chem. lxxiii. 212; Jahresb. 1857, p. 456).—A hot saturated solution of picric acid in *benzene* yields shining light yellow rhombic crystals of the compound $C^6H^6.C^6H^3(NO^2)^3O$, which remains transparent in an atmosphere of benzene, but when exposed to the air immediately begins to give off benzene, and is ultimately reduced to a brittle mass of crystals of picric acid. The compound melts between 85° and 90° to a light yellow liquid. It dissolves without decomposition in alcohol and ether, but cannot be crystallised therefrom. Water abstracts picric acid from it, the whole of the benzene then volatilising at the boiling heat.

*Picrate of Naphthalene*, $C^{10}H^8.C^6H^3(NO^2)^3O$, separates from a hot alcoholic solution of the two substances in gold-yellow needles, which after being rinsed with a little alcohol, may be dried in the air between paper. Cold alcohol or benzene may also be used as the solvent. The compound melts at 149°, dissolves without decomposition in alcohol, ether, and benzene, and is but slowly decomposed by boiling water.

*Picrate of Anthracene*, $C^{14}H^{10}.C^6H^3(NO^2)^3O$, has been already described (p. 351).

The formation of these compounds may serve for the separation of hydrocarbons one from the other. Fritzsche found that coal-tar oil boiling at 150°, and free from acid and alkaline products, gave with picric acid an immediate and abundant precipitate of yellow needle-shaped crystals containing only one hydrocarbon, viz. naphthalene, on further addition of picric acid, a crystallised compound of that acid with a hydrocarbon heavier than water was formed; and the mother-liquor, when cooled to a very low temperature, deposited monoclinic crystals, which when decomposed by ammonia and distilled, yielded a hydrocarbon of variable boiling point, but related to cumene in composition and properties. Other trinitro-acids unite with hydrocarbons in a similar manner.

### *Compounds produced by the action of Reducing Agents on the Nitrophenic Acids.*

### 1. *By Sulphide of Ammonium.*

**Nitrophenamic, Dinitrodiphenamic** or **Amidonitrophenic Acid,** $C^{12}H^{12}N^4O^6 = \left.\begin{matrix}(C^6H^4)^2\\(NO^2)^2\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix} = C^{12}H^6(NH^2)^2(NO^2)^2O^2$. (Laurent and Gerhardt, Compt. chim. 1849, p. 468.)—Formed by the action of sulphide of ammonium on dinitrophenic acid. When dinitrophenate of ammonium is gently heated with sulphide of ammonium, a brisk reaction takes place after a few minutes, and the resulting nearly black mass deposits on cooling large black-brown needles, which may be freed from excess of sulphide of ammonium by boiling with acetic acid, and purified by two or three crystallisations from water.

Nitrophenamic acid thus obtained forms black-brown needles which yield a yellow powder. They are hexagonal prisms with four angles of 131° 30′ and two of 97°. They contain 10 per cent. or 4 at. water ($C^{12}H^{12}N^4O^6.4H^2O$), which they give off between 100° and 110°. The acid is very slightly soluble in cold water, moderately soluble in alcohol and ether. When heated it first gives off its water of crystallisation, then melts, throws off a few colourless scales and a brown oil, and leaves an abundant residue of charcoal which takes fire when strongly heated.

*Nitrophenamate of ammonium* does not appear to have been obtained in the solid state. The acid dissolves in ammonia, forming a deep red solution which gives off all its ammonia during concentration. The *potassium-salt*, $C^{12}H^{11}KN^4O^6$, forms small crystalline nodules very soluble in water and in alcohol. The *barium-salt* forms sparingly soluble brown needles, obtained by adding acetate of barium to an ammoniacal solution of the acid. The *calcium-salt* obtained in like manner separates after a while in small needles. The *copper-salt* is a yellow-green precipitate; the lead-salt an orange-brown precipitate. The *silver-salt*, $C^{12}H^{11}AgN^4O^6$, is a dark brown-yellow precipitate which separates in scales from hot solutions.

**Ethyl-nitrophenidine** or **Nitrophenetidine,** $C^6H^3(C^2H^5)(NH^2)(NO^2)O$. (Cahours, Ann. Ch. Phys. [3] xxvii. 463.)—A base produced by passing sulphydric acid and ammonia gases simultaneously through a solution of ethylic dinitrophenate (p. 399). It crystallises in brown needles resembling methyl-nitrophenidine or nitranisidine (i. 304). It acts on chloride of benzoyl when heated with it, forming a product which crystallises from alcohol in small needles. It forms crystallisable salts with hydrochloric, nitric and sulphuric acids.

**Picramic, Dinitrophenamic,** or **Amido-dinitrophenic Acid,** $C^6H^5N^3O^5 = \left.\begin{matrix}(C^6H^2)''\\(NO^2)^2\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} = C^6H^2(NH^2)(NO^2)^2O$ (Girard, Compt. rend. xxxvi. 421.—Wöhler, Pogg. Ann. xiii. 488.—E. Pugh, Ann. Ch. Pharm. xcvi. 83.)—Produced by the action of sulphide of ammonium or of ferrous salts on picric acid.—1. When sulphydric gas is passed in excess through a saturated alcoholic solution of picric acid neutralised with ammonia, the liquid acquires a deep red colour and deposits a mass of dark red crystals of picramate of ammonium, an additional quantity of which is obtained on distilling off the alcohol; and from this salt the acid may be separated by precipitation with acetic acid from a hot solution (Girard).—2. The *nitrohæmatic acid* which Wöhler obtained by the action of ferrous sulphate on picric acid has been shown to be identical with picramic acid (p. 403).

Picramic acid separated from its ammonium-salt by acetic acid forms beautiful red needles, often grouped in tabular masses (Girard); from an ethereal solution it crystallises in distinct prismatic crystals with very acute terminal faces, garnet-coloured by reflected, yellowish-red by transmitted light (Pugh). It has a slightly bitter taste (Girard); does not taste bitter (Pugh). Melts at 165°, and solidifies in a crystalline mass on cooling (Girard). It is nearly insoluble in *water*, even at the boiling heat, but soluble in *alcohol* and *ether* (Girard).

The acid heated above 165° is decomposed, with evolution of tarry vapours containing hydrocyanic acid and ammonia, and leaves a residue of charcoal (Girard, Wöhler). It burns vividly when thrown on red-hot coals (Girard). It dissolves at ordinary temperatures in *sulphuric acid*, forming a red solution, from which, on dilution with water and addition of ammonia, the picramic acid separates out unaltered: similarly with *hydrochloric acid*; but by hot concentrated sulphuric acid it is decomposed and carbonised (Girard). Strong *nitric acid* decomposes it, with abundant evolution of nitrous fumes, the liquid assuming a straw-yellow colour and the picramic acid being converted into picric acid (Girard, Pugh). According to Wöhler, nitrohæmatic acid is not reconverted into picric acid by the action of nitric acid; and according to Carey Lea, this is also the case with picramic acid.

Picramic acid unites readily with *bases.* Its salts are mostly crystalline; their general formula is $C^6H^4MN^3O^5$. The solutions of the alkaline picrates precipitate the salts of copper, mercury and silver, but not those of manganese, iron, cobalt, or nickel.

*Picramate of ammonium,* $C^6H^4(NH^4)N^3O^5$, prepared as above, separates from the alcoholic solution by spontaneous evaporation, in dark orange-red rhombohedral tables. It does not decompose at 100°, but at 135° it effloresces and gives off ammonia; melts at 165°, and decomposes at a higher temperature. It dissolves readily in water and alcohol, forming deep red solutions, but is insoluble in ether. The aqueous solution is decomposed by continual boiling, with separation of a brown powder. (Girard.)

*Picramate of Copper,* $C^{12}H^8Cu''N^6O^{10}$, is a yellowish-green, amorphous precipitate, which detonates slightly, is insoluble in water and alcohol, but soluble in acids. (Girard.)

*Picramate of Lead* is an orange-coloured powder which explodes when heated, and also by percussion, but without much noise. It dissolves in water, ammonia and acids, but is insoluble in alcohol. (Girard.)

*Picramate of Potassium,* $C^6H^4KN^3O^5$.—Obtained by decomposing the hot solution of the ammonia-salt with potash. Separates on cooling in red transparent elongated rhombic tables, containing 19·9 per cent. potash. It decomposes with slight detonation when somewhat strongly heated, and leaves a residue of charcoal. Dissolves pretty easily in water, sparingly in alcohol. (Girard.)

*Picrate of Barium,* $C^{12}H^8Ba''N^6O^{10}$.—On decomposing a hot solution of picramate of ammonium with nitrate of barium, this salt separates in small silky tufts of red and golden-yellow needles. It bears a heat of 200° without decomposition, but detonates at a higher temperature, leaving a residue of charcoal. Dissolves sparingly in water and alcohol. Contains 27·9 per cent. baryta. (Girard.)

*Picramate of Silver,* $C^6H^4AgN^3O^5$, is obtained by decomposing the ammonia-salt with nitrate of silver, in the form of a brick-red amorphous precipitate, which does not blacken by exposure to light, but decomposes, with blackening, at about 140°, leaving a residue which melts at about 165°. On glowing coals, it burns without detonation. It is insoluble in cold water and in alcohol. Boiling water decomposes it, leaving an insoluble residue. (Girard.)

**Nitrochlorophenamic** or **Amidonitrochlorophenic Acid,** $C^6H^5N^2ClO^3$ = $\left.\begin{matrix}(C^6H^4)''\\ NO^2\\ Cl\\ H\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix} = C^6H^3(NH^2)(NO^2)ClO$. (Griess, Ann. Ch. Pharm. cix. 286.)—When dinitrochlorophenic acid or its ammonium-salt (p. 400) is digested at a gentle heat with sulphide of ammonium, the liquid assumes a blood-red colour and deposits sulphur; and on adding acetic acid to the concentrated filtrate, nitrochlorophenamic acid is precipitated and may be purified by crystallisation from hot water. The crystals dried at the ordinary temperature contain $2C^6H^5N^2ClO^3.H^2O$, but become anhydrous at 100°, assuming at the same time a scarlet colour. The acid has a sweetish taste with bitter aftertaste. When heated it turns red, melts at about 160°, solidifying again at 140° to a brown crystalline mass, and sublimes with partial decomposition. It dissolves but sparingly even in hot water; the hot saturated solution solidifies on cooling to a network of brass-yellow capillary needles. It dissolves easily in *alcohol* and *ether*, also in *sulphuric* and *hydrochloric acids* at ordinary temperatures. Warm concentrated *nitric acid* decomposes it. *Nitrous acid* reduces it to diazonitrochlorophenol (p. 408).

The nitrochlorophenamates of the alkali-metals and alkaline earth-metals are insoluble. The salts are mostly yellow or brown-red, and detonate when heated. The *ammonium-salt*, $C^6H^4(NH^4)N^2ClO^3$, crystallises from the solution of the acid in aqueous ammonia in yellowish-red crystals; its blood-red aqueous solution gives off ammonia when evaporated; so likewise does the solid salt when left over oil of vitriol in rarefied air. The *barium-salt* forms brown-red crystals easily soluble in water. The *lead-salt*, $C^{12}H^8Pb''N^4Cl^2O^6$, is obtained by adding neutral lead-acetate to the solution of the ammonium-salt, as a brown-red precipitate. The ammonium-salt gives a yellowish-green precipitate with *cupric sulphate,* yellow with *mercuric chloride*, brown-red with *nitrate of silver.*

### 2. *By Hydriodic Acid and Stannous Chloride.*

Picric acid treated with either of these reagents, yields a salt of picramine (*q. v.*); see also p. 403.

### 3. *By Cyanide of Potassium.*

Picric acid treated with this reagent is converted into isopurpuric or picrocyamic acid, already described (iii. 433).

*Metapurpuric acid.* $C^8H^4N^4O^4$.—This acid, related to dinitrophenic acid in the same manner as isopurpuric to picric acid, is obtained as a potassium-salt, when an aqueous or alcoholic solution of dinitrophenic acid is added by drops to a solution of cyanide of potassium heated to 60°. A dark coloured crystalline powder is then precipitated, which may be purified by washing with a little cold water, recrystallising from hot water, pressing, and drying over oil of vitriol. *Metapurpurate of potassium* thus obtained is a dark red substance, exhibiting metallic lustre, and dissolving with deep crimson colour in water and in alcohol. The solutions have the odour of cyanic acid. The analysis of the salt leads to the formula $C^8H^4KN^4O^4.H^2O$. It becomes anhydrous when heated. The solution gives dark brown precipitates with the chlorides of barium and strontium, and with most metallic solutions. The *silver-salt* is red, with green metallic lustre. The acid itself has not been isolated. (Pfaundler and Oppenheim, Bull. Soc. Chim. [2] iv. 99.)

### 4. *By Nitrous Acid.* DIAZONITROPHENOLS.

*a.* **Diazonitrophenol.** $C^6H^3N^3O^3 = C^6H^3N^2(NO^2)O$. (Griess, Ann. Ch. Pharm. cxiii. 201.)—Produced by passing nitrous acid vapour into an ethereal solution of nitrophenamic acid (p. 406):

$$C^6H^6N^2O^3 + HNO^2 = C^6H^3N^3O^3 + 2H^2O.$$

It then separates as a brownish-yellow granular mass, and is obtained in the same form, recrystallised from alcohol. It yields a light yellow powder turning red on exposure to light; explodes with great violence when heated to 100°. It dissolves easily in *alcohol*, slowly and with partial decomposition in hot *water*, a red amorphous powder then separating, and the filtrate on cooling depositing diazonitrophenol in small yellow prisms. It dissolves without decomposition in cold *hydrochloric* and *sulphuric acids*. When boiled with *fuming nitric acid*, it forms a compound which separates in yellow flocks on addition of water. On adding *carbonate of potassium* to the alcoholic solution of diazonitrophenol and applying a gentle heat nitrogen is evolved, and the residue left on evaporating the alcohol yields with acids a brown-red amorphous precipitate which might be expected to exhibit the composition of nitrophenic acid, $C^6H^5NO^3$ (see the corresponding decomposition of diazodinitrophenol, *infra*), but is in reality different both from that compound and from its isomer, isonitrophenic acid (pp. 394, 395).

**Diazodinitrophenol.** $C^6H^2N^4O^5 = C^6H^2N^2(NO^2)^2O$. (Griess, *loc. cit.*)—Produced by passing nitrous acid gas into an alcoholic solution of picramic acid:

$$C^6H^5N^3O^5 + HNO^2 = C^6H^2N^4O^5 + 2H^2O.$$

If however the picramic acid used is impure, or if it be added to alcohol previously saturated with nitrous acid and slightly warmed, nothing but dinitrophenic acid is obtained.

Diazodinitrophenol crystallises in brass-yellow or golden-yellow laminæ, sparingly soluble in *water*, *alcohol*, and *ether*; is neutral to vegetable colours; has a bitter taste; and detonates violently when heated. It is dissolved without decomposition by *mineral acids*, but is decomposed when heated with *fuming sulphuric acid*; dry *chlorine* does not act upon it. When boiled for some time with water, it is decomposed, with formation of a resinous body, and a red-brown pulverulent substance soluble in alcohol, ether and alkalis, but not crystal isable. On adding *carbonate of potassium* to the alcoholic solution of diazodinitrophenol, nitrogen is evolved and dinitrophenic acid is produced, the colour of the liquid changing from yellow to red:

$$C^6H^2N^4O^5 + H^2O = C^6H^4(NO^2)^2O + N^2 + O.$$

The oxygen set free, according to this equation, is probably consumed in oxidising the alcohol.

**Diazonitrochlorophenol.** $C^6H^2N^3ClO^3 = C^6H^2N^2(NO^2)ClO$. (Griess, *loc. cit.*) This compound is formed when a rapid stream of nitrous acid gas is passed through a slightly warmed solution of nitrochlorophenamic acid, or when the latter is added to alcohol previously saturated with nitrous acid. By recrystallisation from alcohol, it is obtained in large brown-red prismatic crystals. It is sparingly soluble in *alcohol*, *ether* and hot *water*, crystallises from hot water in greenish gold-yellow laminæ, from ether in furcate groups of needles. It dissolves in *sulphuric acid*, and separates from the solution after addition of water, in long thread-like crystals, and is soluble without decomposition in acids in general. It yields a yellow powder turning red on exposure to light; detonates violently above 100°; and when mixed in alcoholic solution with alkalis, gives off nitrogen and yields nitrochlorophenic acid.

*Appendix to Phenol-derivatives.*

**Tri-iodophenic acid.** $C^6H^3I^3O$.—Obtained by treating phenol with a considerable quantity of protochloride of iodine. On dissolving the product in soda and acidulating with sulphuric acid, a precipitate is obtained consisting of mono-, di-, and tri-iodophenic acids, from which the two former may be extracted by boiling alcohol of 60 per cent. The residue dissolves slowly in strong alcohol at the boiling heat, and the solution when evaporated deposits tri-iodophenic acid in radiate groups of yellow crystals. It is easily soluble in ether, and decomposes when heated, with copious disengagement of iodine. Treated with excess of protochloride of iodine, it yields pentachlorophenic acid (p. 393), which may be sublimed in splendid white needles. (Schützenberger, Bull. Soc. Chim. [2] iv. 102.)

**PHENOL-BLUE.** Also called *Azulin.* A blue dye obtained by heating pæonin (p. 324) with aniline. (See Hofmann's *Report on Chemical Products &c. in the Exhibition of* 1862, p. 135.)

**PHENOXACETIC ACID.** Syn. with PHENYLGLYCOLLIC ACID. (See GLYCOLLIC ETHERS, ii. 918.)

**PHENYL.** $C^6H^5$. In the free state $C^{12}H^{10}$.—The radicle of phenol or phenylic alcohol: known also in the form of chloride, bromide, acetate, &c. It is obtained in the free state: 1. By the action of sulphuric acid on a colourless oil (probably phenylic oxide $(C^6H^5)^2O$, p. 416), resulting, among other products, from the dry distillation of cupric benzoate (List and Limpricht, Ann. Ch. Pharm. xc. 209).—2. By the action of sodium on phenylic bromide or bromobenzene (Fittig, *ibid.* cxxi. 361; cxxxii. 201), or of sodium-amalgam on phenylic chloride (Church, Chem. Soc. J. xvi. 76). Fittig prepares it as follows:—A mixture of benzene and bromine in equivalent proportions is exposed in a retort to diffused daylight for eight to fourteen days or as long as white fumes of hydrobromic acid continue to appear; the contents of the retort are then distilled into a receiver; the distillate is shaken with soda-ley till it becomes colourless; the watery liquid is removed; and the oil carefully dried with chloride of calcium and rectified, collecting apart the portion which passes over below 160°. This distillate, consisting of benzene and monobromobenzene or phenylic bromide, is mixed in a retort with an excess of sodium cut into thin slices; the retort is left to stand for 24 hours in cold water; and the product distilled off. The distillate is easily resolved by one rectification into benzene and pure phenyl, which immediately solidifies. It is important that the mixture of benzene and phenylic bromide be completely dehydrated before treating it with sodium, otherwise the hydrogen evolved from the water will unite with the nascent phenyl and convert a portion of it into benzene. A mixture of pure phenylic bromide with an equal volume of anhydrous ether may also be used instead of the mixture of phenylic bromide and benzene, but it is less advantageous.

3. Phenyl is also produced, together with benzene and other products, by the action of alcoholic potash on nitrate of azophenylamine (p. 432):

$$\underset{\substack{\text{Azophenyl-}\\\text{amine.}}}{2C^6H^4N^2} + \underset{\text{Alcohol.}}{C^2H^6O} = \underset{\text{Phenyl.}}{C^{12}H^{10}} + \underset{\text{Aldehyde.}}{C^2H^4O} + N^4.$$

On heating the mixture in a retort, benzene passes over with the alcohol and afterwards the phenyl, which condenses in the receiver as a crystalline mass, and may be purified by repeated crystallisation from alcohol. (Griess, Phil. Trans. 1864 [3] 692.)

4. Together with other products, by heating sulphate of diazobenzidine (p. 412) with alcohol. (Griess.)

Phenyl crystallises from alcohol in iridescent, nacreous scales which melt at 69° and sublime at a higher temperature (List and Limpricht); in shining laminæ melting at 70·5° (Fittig), 70° (Griess), and boiling between 239° and 240° (Fittig). It gives by analysis 93·75 per cent. carbon and 6·25 hydrogen (List and Limpricht); 93·24 carbon and 6·55 hydrogen (Fittig), the formula $C^{12}H^{10}$ requiring 93·51 carbon and 64·9 hydrogen.*

It is converted by bromine, with evolution of hydrobromic acid, into bromophenyl, $C^{12}H^8Br^2$, and by fuming nitric acid into nitrophenyl, $C^{12}H^8(NO^2)^2$.

The formation of these compounds shows that the formula of phenyl in the free state is not $C^6H^5$, but $C^{12}H^{10}$; for if it were $C^6H^5$, that of bromophenyl would be $C^6H^4Br$, and that of nitrophenyl, $C^6H^4(NO^2)$; but these formulæ are inadmissible, because the sum of the hydrogen- and bromine-atoms in the one case and of the hydrogen- and nitrogen-atoms in the other is uneven. In this respect then phenyl in the free state agrees with the other so-called alcohol-radicles. methyl, ethyl, &c. Fittig however regards the compound $C^{12}H^{10}$, obtained as above, as bearing only a distant relationship to the radicle of the phenyl-compounds, and accordingly designates it by a different name, viz. diphenyl, on the ground that the compounds formed from it by the action of bromine and nitric acid do not belong to the same series as phenylic alcohol and its derivatives. In this respect however phenyl does not differ essentially from methyl, ethyl, and their homologues, inasmuch as none of these bodies are found to yield, by combination or substitution, compounds belonging to the same series as the alcohol from which they are supposed to be derived: methyl, $C^2H^6$, for example, when treated with chlorine yields, not methylic chloride, $CH^3Cl$, but ethylic chloride, $C^2H^5Cl$, and monochlorinated ethylic chloride, $C^2H^4Cl^2$, a compound related to methyl, $C^2H^6$, exactly in the same manner as dibromophenyl, $C^{12}H^8Br^2$, is related to phenyl, $C^{12}H^{10}$. If, as Schorlemmer's experiments seem to show, all the so-called alcohol-radicles in the free state are really hydrides, the so-called phenyl or diphenyl must be regarded as the hydride of the radicle $C^{12}H^9$.

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* List and Limpricht assigned to their product the formula $C^{10}H^8$, which however does not agree so well with their analysis as that of phenyl, $C^{12}H^{10}$, requiring 93·41 per cent. C, and 6·66 H.

**Bromophenyl.** $C^{12}H^8Br^2$. *Dibromodiphenyl.* (Fittig, Ann. Ch. Pharm. cxxxii. 204.)—This compound is produced:—1. By saturating phenyl with excess of bromine under water till it forms a doughy mass, removing the excess of bromine by washing with soda-ley and crystallising the now solid product from boiling benzene (Fittig).—2. By heating perbromide of diazobenzidine (p. 412) with carbonate of sodium, or boiling it with alcohol (Griess):

$$C^{12}H^8N^4.H^2Br^2.Br^4 = C^{12}H^8Br^2 + N^4 + Br^4.$$

It forms concentric groups of rather large colourless prisms having a splendid lustre and strong refracting power, insoluble in *water* and in cold *alcohol*, sparingly soluble in boiling *alcohol*, easily in *benzene*. It melts at 164° to a colourless liquid which may be cooled below 150° without solidifying; at a higher temperature it distils without decomposition. It is not attacked by alcoholic potash or potassic acetate, even after prolonged boiling, and therefore does not exhibit the characters of bromide of chrysene, $C^{12}H^8.Br^2$; neither can this hydrocarbon be separated from it by the action of sodium.

**Chlorophenyl.** $C^{12}H^8Cl^2$. *Dichlorodiphenyl.*—Produced by heating the chloroplatinate of diazobenzidine (p. 412) in a retort, with 4 to 6 times its weight of sodic carbonate. A copious evolution of gas then takes place, and chlorophenyl distils over as an oily body which solidifies to a white mass in the neck of the retort, and may be purified by recrystallisation from boiling alcohol:

$$C^{12}H^8N^4.H^2Cl^2.PtCl^4 = C^{12}H^8Cl^2 + Cl^4 + Pt + N^4.$$

It crystallises in white, usually well-developed prisms, insoluble in *water*, sparingly soluble in *alcohol* even at the boiling heat, but readily soluble in *ether*. It melts at 148° to a yellowish oil, which can be distilled without decomposition. (Griess, Phil. Trans. 1864, Pt. iii. p. 730.)

**Nitrophenyl.** $C^{12}H^8(NO^2)^2$. *Dinitrodiphenyl.* (Fittig, Ann. Ch. Pharm. cxxiv. 275.)—A solution of phenyl in fuming nitric acid solidifies to a mass of needle-shaped crystals consisting chiefly of this compound. It is purified by filtering the liquid through gun-cotton, washing the remaining crystalline mass with water, boiling it with small quantities of alcohol, as long as the liquid is coloured yellow thereby, and crsytallising the white mass five or six times from alcohol, taking care that a small portion remains each time undissolved. When thus purified it crystallises in long colourless needles, which melt at 213° and decompose, with separation of charcoal, at a stronger heat. It is quite insoluble in water, and very sparingly soluble in alcohol. By covering it with alcohol and sulphide of ammonium, and passing sulphydric acid gas through the liquid till the whole of the nitrophenyl is dissolved, it is converted into amidonitrophenyl $C^{12}H^8(NH^2)(NO^2)$, and amidophenyl $C^{12}H^8(NH^2)^2$, which is identical with Zinin's benzidine (i. 544), the former or the latter predominating according as the decomposition takes place in a cold or a hot solution. These two bases are easily separated from one another, as the latter only is soluble in hot water, alcohol or hydrochloric acid, and is almost wholly precipitated from these solutions by sulphuric acid.

*Isonitrophenyl*, $C^{12}H^8(NO^2)^2$.—This compound, formed, simultaneously with the nitrophenyl above described, by the action of fuming nitric acid on phenyl, remains in the mother-liquor after the latter has crystallised out. On mixing the acid filtrate with water, a soft yellowish-white mass separates, which by repeated crystallisation from alcohol, may be resolved into liquid nitrobenzene and crystalline isodinitrophenyl.

The latter is insoluble in *water*, easily soluble in hot *alcohol*. It is distinguished from nitrophenyl by melting at a much lower temperature, viz. at 93·5°, and by forming with reducing agents two bases differing in properties from the two just described, though agreeing with them in composition. (Fittig, *loc. cit.*)

**Bromonitrophenyl.** $C^{12}H^6Br^2(NO^2)^2$. *Dibromodinitrodiphenyl.* (Fittig, Ann. Ch. Pharm. cxxxii. 206.)—Bromophenyl, gently heated with fuming nitric acid, dissolves with somewhat strong reaction, and after a few minutes the whole solidifies to a pulp of fine needle-shaped crystals of this compound, which, after washing with water, may be crystallised from hot benzene. It is perfectly insoluble in *water*, very sparingly soluble in *alcohol* even at the boiling heat, more easily in hot *benzene*, whence it crystallises in splendid slightly yellow capillary needles, often an inch long. It is very much like dinitrophenyl in external appearance, and cannot be volatilised without decomposition.

*Bases produced by reduction of the preceding Nitro-compounds.*

**Amidophenyl,** $C^{12}H^{12}N^2 = C^{12}H^8(NH^2)^2$ or **Benzidine,** $\left.\begin{matrix}(C^{12}H^8)''\\ H^4\end{matrix}\right\}N^2$.—This compound is obtained by evaporating the solution of nitrophenyl after prolonged treatment with sulphydric acid, as above described, dissolving the residue in dilute hydrochloric acid, and precipitating with sulphuric acid. The sulphate thus separated is decomposed by boiling with ammonia, and the free base is purified by re-solution in hot water, precipitation with sulphuric acid and separation by ammonia, and finally, recrystallised from hot water. It crystallises in colourless shining scales which melt at 118° (not at 108° as generally stated).[*] (Fittig, Ann. Ch. Pharm. cxxiv. 275.)

**Amidonitrophenyl,** $C^{12}H^{10}N^2O^2 = C^{12}H^8(NH^2)(NO^2) = \left.\begin{matrix}[C^{12}H^8N'']''\\ H^3\end{matrix}\right\}\begin{matrix}N\\ O^2\end{matrix}$, is obtained by evaporating the above-mentioned solution of nitrophenyl after treatment with sulphydric acid, and boiling the residue with water till the resulting solution no longer gives a precipitate (of benzidine) with sulphuric acid. The residual amidonitrophenyl is dissolved in moderately dilute hydrochloric acid, the liquid is filtered to separate sulphur, then precipitated by ammonia, and the bulky red flocks thus obtained are washed with water and dissolved in hot alcohol. On adding hot water to the alcoholic solution till it begins to show turbidity, amidonitrophenyl separates as a crystalline powder, which is purified by several repetitions of this treatment, and finally recrystallised from hot alcohol. It forms small, bright-red, needle-shaped crystals, melts at about 160°, volatilises with partial decomposition at a higher temperature, dissolves sparingly in *water*, but easily and with red colour in boiling *alcohol*. Its solution in hot strong *hydrochloric acid* is nearly colourless, but turns red on cooling and deposits the free base again when evaporated. The *platinum-salt*, $C^{12}H^{10}N^2O^2.H^2Cl^2.Pt^{iv}Cl^4$, is a flocculent, very easily decomposible precipitate. (Fittig, *loc. cit.*)

**Bromamidophenyl** or **Bromobenzidine,** $C^{12}H^{10}Br^2N^2$.—This base cannot be prepared by reducing nitrobromophenyl with sulphide of ammonium, this reaction yielding nothing but brown resinous products insoluble in hydrochloric acid. But when the nitro-compound is heated with tin and strong hydrochloric acid, it dissolves after some time, and on diluting the solution with water, and filtering, the filtrate deposits after a while hard nodular groups of crystals consisting of a compound of hydrochlorate of bromobenzidine with stannous chloride; which when boiled with dilute aqueous ammonia yields bromobenzidine as a faintly yellow oil which solidifies to a glutinous mass on cooling, and may be separated from stannous oxide by solution in alcohol, whence it separates in hemispherical groups of small hard crystals, very much like sugar-candy, but always having a yellow or brown colour arising from partial oxidation taking place in the alcoholic solution. It is insoluble in water, melts at 89° and decomposes at higher temperatures, with evolution of hydrobromic acid and separation of much charcoal. It is a much weaker base than benzidine.

*Hydrochlorate of bromobenzidine* is obtained in small colourless prisms on dissolving the base in dilute hydrochloric acid and mixing the solution with strong hydrochloric acid. It is partially decomposed by solution in water, and appears also to lose a portion of its acid on mere exposure to the air. Ammonia added to the solution throws down bromobenzidine as a pure white amorphous precipitate. The *chloroplatinate* is a brown amorphous precipitate which cannot be purified by recrystallisation. The *sulphate* is soluble in water; dilute sulphuric acid does not form any precipitate in a solution of the hydrochlorate. (Fittig, Ann. Ch. Pharm. cxxxii. 207.)

A body isomeric with bromobenzidine (probably bromide of azobenzene), is obtained by the direct action of bromine on azobenzene, $C^{12}H^{10}N^2$. This product is sparingly soluble in alcohol and ether; crystallises from alcohol in needles having a faint yellow colour and golden lustre; melts at about 205°, and sublimes in needles. When heated with nitric acid of specific gravity 1·42, it dissolves completely, and the solution on cooling deposits the compound $C^{12}H^8(NO^2)N^2Br^2$ in straw-yellow needles, which are very soluble in alcohol, and melt at about 159° to a liquid which soon boils and decomposes at a higher temperature. (A. Werigo, Ann. Ch. Pharm. cxxxv. 178.)

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[*] The statement found in most Manuals of Chemistry, and at page 545 vol. i. of this work, that benzidine melts at 108°, appears to have originated in a misprint in Zinin's paper (J. pr. Chem. xxxvi. 93). See *Gmelin's Handbook*, x. 339.

**Diazobenzidine,** $C^{12}H^6N^4 = \left.\begin{matrix}(C^{12}H^8\tilde{N}^2)'' \\ H^4\end{matrix}\right\}N^2$. *Tetrazodiphenyl.* (Griess, Phil. Trans. 1864, Pt. iii. p. 719.)—A base obtained as a nitrate by the action of nitrous acid on nitrate of benzidine:

$$C^{12}H^{12}N^2 + 2NHO^2 = C^{12}H^6N^4 + 4H^2O.$$

When nitrous acid vapour is passed through an alcoholic solution of nitrate of benzidine a brown amorphous body separates in considerable quantity (from an aqueous solution only traces are deposited); and on mixing the filtrate with twice its volume of strong alcohol and adding ether, nitrate of diazobenzidine is precipitated in minute crystals, which may be purified by dissolving them in a very small quantity of water, and reprecipitating with alcohol and ether.

*Nitrate of Diazobenzidine*, $C^{12}H^6N^4.2NHO^3$, crystallises in white or slightly yellow needles, easily soluble in *water*, less soluble in *alcohol*, insoluble in *ether*. When heated they explode with violence. The aqueous solution left in a cold place gradually undergoes spontaneous decomposition, and on heating it, nitrogen is evolved, and diphenyl-alcohol (or rather diphenylenic alcohol) $C^{12}H^{10}O^2 = \left.\begin{matrix}(C^{12}H^8)'' \\ H^2\end{matrix}\right\}O^2$, is deposited in white crystals, together with a brown amorphous substance:

$$C^{12}H^6N^4.2NHO^3 + 2H^2O = C^{12}H^{10}O^2 + 2NHO^3 + N^4.$$

(See PHENYLENIC ALCOHOLS.)

*Perbromide of Diazobenzidine*, $C^{12}H^6N^4.2HBr.Br^4$, is precipitated on adding bromine-water to an aqueous solution of the nitrate, in round reddish crystals, which must be washed on a filter with water, and quickly dried over oil of vitriol and quicklime. It is very unstable, gradually giving off bromine even at ordinary temperatures. It is also decomposed, with evolution of gas, by solution in *alcohol*. Heated with *carbonate of sodium*, it gives off bromine and nitrogen, and leaves bromophenyl (p. 410):

$$C^{12}H^6N^4.2HBr.Br^4 = C^{12}H^8Br^2 + Br^4 + N^4.$$

By aqueous *ammonia* it is converted into bromide of ammonium and tetrazodiphenylimide:

$$\underset{\text{Perbromide.}}{C^{12}H^6N^4.2HBr.Br^4}[*] + 8NH^3 = \underset{\text{Tetrazodiphenylimide.}}{\left.\begin{matrix}(C^{12}H^6N^4)^{iv} \\ H^2\end{matrix}\right\}N^2} + 6NH^4Br.$$

The tetrazodiphenylimide is deposited in crystals, and by repeated crystallisation from strong alcohol may be obtained in small, very brilliant, white or yellowish plates, insoluble in water, very sparingly soluble in cold, easily in boiling alcohol, moderately in ether. It melts at 127° to a yellow oil, which is decomposed with slight explosion at a higher temperature. It is neutral to test-paper, does not combine with acids or alkalis, is not altered by boiling with strong hydrochloric acid, or with aqueous or alcoholic potash, but is decomposed by nitric or by strong sulphuric acid.

*Platinochloride of Diazobenzidine*, $C^{12}H^6N^4.2HCl.Pt^{iv}Cl^4$, is precipitated by platinic chloride from a solution of the nitrate or sulphate, in light yellow, very small narrow plates, or from very dilute solutions in small elongated, well-formed hexagonal plates. It is almost insoluble in *water*, *alcohol* and *ether*. Exposure to light during drying causes the crystals to turn brown. Heated with *carbonate of sodium* it gives off nitrogen and chlorine, together with chlorophenyl (p. 410) which passes over as an oil, and solidifies as a white mass in the neck of the retort:

$$C^{12}H^6N^4.2HCl.PtCl^4 = C^{12}H^8Cl^2 + Pt + Cl^4 + N^4.$$

*Sulphate of Diazobenzidine*, $C^{12}H^6N^4.3SH^2O^4$.—On mixing a concentrated aqueous solution of the nitrate with cold sulphuric acid, previously diluted with its own bulk of water, and then adding strong alcohol, this salt separates either as a white crystalline powder, or in white needles; if alcohol does not precipitate it completely, ether must be added. It is very soluble in water, and explodes when heated.

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[*] Neglecting the hydrobromic acid, the compound may be regarded as the bromide of a tetratomic radicle $(C^{12}H^6N^4)^{iv}Br^4$.

Heated with *alcohol* it is violently decomposed, giving off nitrogen, sulphuric acid and aldehyde, and yielding white crystals of phenyl (p. 410):

$$\underset{\text{Sulphate of Diazo-benzidine.}}{2(C^{12}H^{6}N^{4}.3SH^{2}O^{4})} + \underset{\text{Alcohol.}}{4C^{2}H^{6}O} = \underset{\text{Phenyl.}}{2C^{12}H^{10}} + \underset{\text{Aldehyde.}}{4C^{2}H^{4}O} + N^{8} + 6SH^{2}O^{4}.$$

On heating a solution of the sulphate in a small quantity of oil of vitriol, a violent evolution of nitrogen takes place, and a brown liquid is formed containing a trisulpho- and a tetrasulpho-acid:

$$C^{12}H^{6}N^{4} + 3SH^{2}O^{4} = C^{12}H^{6}.3SH^{2}O^{4} + N^{4}.$$
$$C^{12}H^{6}N^{4} + 4SH^{2}O^{4} = C^{12}H^{6}.4SH^{2}O^{4} + N^{4}.$$

On boiling the brown liquid with thirty times its volume of water, saturating with carbonate of barium, evaporating the filtrate to dryness over the water-bath, and exhausting the residue several times with water, the barium-salt of the trisulpho-acid dissolves while that of the tetrasulpho-acid remains behind. (See SULPHURIC ETHERS.)

**Diazobenzidine-Aniline** or **Diazodiphenylene-diphenyl-tetramine,**

$$C^{24}H^{20}N^{6} = C^{12}H^{6}N^{4}.2C^{6}H^{7}N = \left.\begin{matrix}(C^{12}H^{8}\overset{\prime\prime\prime}{N}^{2})''\\(C^{6}H^{5})^{2}\\H^{2}\end{matrix}\right\}N^{4}.\quad \textit{Tetrazodiphenyl-amidobenzol.}$$

—This compound separates on adding aniline to aqueous nitrate of diazobenzidine, as a yellow crystalline mass, which may be purified by repeated washing with alcohol:

$$C^{12}H^{6}N^{4}.2NHO^{3} + 4C^{6}H^{7}N = C^{24}H^{20}N^{6} + 2(C^{6}H^{7}N.NHO^{3}).$$

It is insoluble in water, and very sparingly soluble even in boiling alcohol and ether, from which however it separates in lance-shaped crystals, generally united in stellate groups. It explodes when heated, and decomposes, with evolution of nitrogen, when boiled with mineral acids. (Griess.)

**PHENYL, BROMIDE OF.** $C^{6}H^{5}Br$. See MONOBROMOBENZENE, under PHENYL, HYDRIDE OF (p. 414).

**PHENYL, CHLORIDE OF.** $C^{6}H^{5}Cl$. See MONOCHLOROBENZENE, under PHENYL, HYDRIDE OF (p. 414).

**PHENYL, CYANIDE OF.** $C^{6}H^{5}.CN$, or *Benzonitrile*, $C^{7}H^{5}N$.—Already described under the latter name (i. 563).—Mendins has shown (Ann. Ch. Pharm. cxxi. 129; Jahresb. 1862, p. 324), that when treated with hydrochloric acid and granulated zinc, it is converted, by the action of the nascent hydrogen thereby evolved, into a base $C^{7}H^{9}N$, isomeric with benzylamine (toluidine), methylaniline, and lutidine, but differing in its properties from all three. This base is an oil lighter than water, having an aromatic not unpleasant odour, boiling between 182·5° and 187·5°, soluble in water, miscible in all proportions with alcohol and ether. The aqueous solution becomes turbid at the heat of the hand, from separation of a portion of the dissolved oil. It is not coloured by *chloride of lime;* when evaporated with *nitric acid*, it emits the odour of bitter almond oil. When exposed to the air it is quickly converted into small shining needles of the carbonate. It forms thick white fumes with hydrochloric acid. The *hydrochlorate*, $C^{7}H^{9}N.HCl$, is infusible, sublimable, easily soluble in water and alcohol, insoluble in ether, and crystallises in rather large square plates. The *chloroaurate* crystallises in long yellow needles; the chloromercurate from alcohol in radiate groups of needles; the *chloroplatinate*, $2C^{7}H^{10}NCl.Pt^{iv}Cl^{4}$, in very thin plates.

**PHENYL, HYDRATE OF.** See PHENOL (p. 289).

**PHENYL, HYDRIDE OF.** $C^{6}H^{5}H$.—Syn. with BENZENE, under which name it has been already described, together with several of its derivatives (i. 541). We have here to notice several new derivatives of benzene, and some additional observations on those already described.

### *Azo- and Amido-benzenes.*

Aniline or monophenylamine, $C^{6}H^{7}N$, is regarded by Griess as amidobenzene $C^{6}H^{5}(NH^{2})$, and by the action of nitrous acid on aniline and its salts, compounds are formed containing the bases $C^{6}H^{4}N^{2}$ and $C^{12}H^{11}N^{3}$. The former is regarded by Griess as diazobenzene, that is, as formed from benzene, $C^{6}H^{6}$, by the substitution of 2 atoms of nitrogen for 2 at. hydrogen; the latter as a compound of diazobenzene with amidobenzene (aniline) $= C^{6}H^{4}N^{2}.C^{6}H^{5}(NH^{2})$. The compound $C^{6}H^{4}N^{2}$ may however also be regarded as azophenylamine $\left.\begin{matrix}(C^{6}H^{4}N''')'\\H^{2}\end{matrix}\right\}N^{2}$, that as monophenylamine having 3 at. hydrogen replaced by 1 at. nitrogen; and the compound $C^{12}H^{11}N^{3}$, in like manner as azodiphenyl-diamine $\left.\begin{matrix}(C^{12}H^{7}N''')''\\H^{4}\end{matrix}\right\}N^{2}$. Viewed in this light they will be described, together with their bromo-, chloro-, and nitro-derivatives, under PHENYLAMINES.

### *Bromobenzenes.*

**Monobromobenzene,** $C^6H^5Br$.—This compound, obtained by the action of bromine on benzene (i. 542), appears to be identical with bromide of phenyl produced by the action of bromide of phosphorus on phenol. Fittig's mode of preparing it from benzene has been already given under Phenyl (p. 409). To separate it from unaltered benzene, the mixture of the two, obtained as above, is rectified, and the portion which distils between 152° and 154° is collected apart. Riche (Ann. Ch. Pharm. cxxi. 357), by distilling 120 pts. of phenol with 90 pts. bromide of phosphorus, obtained an oily distillate having a sweetish taste like that of chlorobenzene, boiling between 158° and 166°, and containing somewhat less carbon than that required by the formula $C^6H^5Cl$; but it was evidently impure.

Monobromobenzene or bromide of phenyl is not attacked by caustic potash, cyanide of potassium or acetate of silver; with sodium it yields phenyl, $C^{12}H^{10}$, according to Fittig, benzene according to Riche; but the production of benzene probably arose from the presence of moisture (p. 409).

**Dibromobenzene,** $C^6H^4Br^2$, is obtained, mixed however with tribromobenzene, by the action of bromine in excess on benzene (Couper, i. 543). A purer product is obtained by heating the bromoplatinate or the perbromide of azobromophenylammonium (see Phenylamines), either alone, or better with carbonate of sodium:

$$\underset{\text{Bromoplatinate.}}{2(C^6H^5BrN^2.2HBr).PtBr^4} \quad = \quad \underset{\text{Dibromobenzene.}}{2C^6H^4Br^2} + Pt + N^4 + Br^4.$$

$$\underset{\text{Perbromide.}}{C^6H^4BrN^2Br^3} \quad = \quad \underset{\text{Dibromobenzene.}}{C^6H^4Br^2} + N^2 + Br^2.$$

A still better method is to decompose the perbromide with alcohol; the decomposition is complete after a few minutes' boiling, and if too much alcohol has not been used, a large portion of the dibromobenzene separates at once in crystals; the remainder is precipitated on addition of water as thick oil, which soon solidifies to a crystalline mass. After washing with a little alcohol and pressure between bibulous paper, this mass, together with the crystals first precipitated, is subjected to distillation; dibromobenzene then distils over as a colourless oil, which speedily solidifies.

Dibromobenzene crystallises from ether in rectangular prisms or small plates (Griess), oblique prisms (Couper); melts at 89° (Couper, Griess), and boils at 219° (Couper). It has an aromatic odour. (Griess.)

**Tribromobenzene,** $C^6H^3Br^3$, has been already described (i. 543).

**Tetrabromobenzene,** $C^6H^2Br^4$, has recently been obtained by Riche and Bérard (Ann. Ch. Pharm. cxxxiii. 51) as follows:—Dibromobenzene is prepared by exposing benzene to the action of bromine in a long-necked flask, so that no bromine may be lost, and the resulting crystalline mass is heated with excess of bromine to 150° in sealed tubes till the tubes become filled with small crystals. These, which consist of tetrabromobenzene, are separated, by recrystallisation from alcohol in which they are but slightly soluble, from undecomposed dibromobenzene which dissolves easily in that liquid. Tetrabromobenzene forms beautiful, silky, very white crystals, solidifies from fusion at about 160°, and volatilises in flocks.

The bromobenzenes are attacked by fuming nitric acid, yielding the corresponding nitrobromobenzenes (p. 405).

### *Chlorobenzenes.*

**Monochlorobenzene.** $C^6H^5Cl$.—This compound, produced by the action of chlorine or chloride of iodine on benzene (Hugo Müller, Chem. Soc. J. xv. 41; Fittig, Ann. Ch. Pharm. cxxxiii. 49), appears to be identical with chloride of phenyl, obtained by the action of pentachloride of phosphorus on phenol. (Laurent and Gerhardt, Ann. Ch. Pharm. lxxv. 79; Williamson and Scrugham, Chem. Soc. Qu. J. vii. 238; Riche, Ann. Ch. Pharm. cxxi. 357.)

*Preparation.* 1. From *Benzene.*—Benzene absorbs a small quantity of chlorine, and if it be exposed to light or heated to the boiling point, hydrochloric acid is slowly evolved, and two series of products are obtained, viz. chlorides of benzene $C^6H^6Cl^2$, $C^6H^6Cl^4$, $C^6H^6Cl^6$, and chlorobenzenes $C^6H^5Cl$, $C^6H^4Cl^2$, $C^6H^3Cl^3$, the former being produced in larger quantities than the latter. But when chlorine is passed into benzene containing iodine in solution, a much more copious evolution of hydrogen takes place, and chlorobenzene, $C^6H^5Cl$, is produced in much larger quantity, together with the other two substitution-products just mentioned; if the chlorine is in excess, a beautifully crystallised compound is likewise formed. (Hugo Müller.)

2. From *Phenol.*—When 2 at. pentachloride of phosphorus are added by small portions to 5 at. phenol, a violent action takes place at first, great heat being produced and hydrochloric acid evolved; but this action soon ceases and it becomes necessary to

heat the mixture. If it be then distilled upwards till it has nearly ceased to give off hydrochloric acid, and the distillate subsequently collected, about $\frac{2}{3}$ of the whole distils over below 240°, and the temperature then rapidly rises above the range of the mercurial thermometer. The distillate collected below 240° is a limpid colourless liquid, which when washed with hot water and subsequently with potash, yields a thick oil which settles to the bottom of the vessel; and on submitting this oil to fractional distillation, collecting apart the portion which passes over at 136° to 138°, chloride of phenyl is obtained, nearly pure but in small quantity. The brown liquid which distils above the range of the thermometer is phosphate of phenyl, and constitutes by far the largest portion of the product. When an excess of chloride of phosphorus is used in the preparation, the quantity of phenylic chloride obtained appears to be still smaller than with the above proportions.

Chloride of phenyl (obtained by the second process) is a colourless mobile liquid, boiling at 136° (W. and S.), at 137° (Riche). According to Laurent and Gerhardt, it is converted by water, and more quickly by aqueous potash, into phenol:

$$C^{12}H^5Cl \quad + \quad H^2O \quad = \quad HCl \quad + \quad C^6H^6O;$$

but according to Riche (Ann. Ch. Pharm. cxxx. 256), it is not attacked by potash, not even when heated with alcoholic potash in a sealed tube: hence he regards the compound obtained as above, not as chloride of phenyl, but as monochlorobenzene.

Pure chlorobenzene prepared by Müller's process is likewise, according to Fittig (Ann. Ch. Pharm. cxxxiii. 50), perfectly indifferent to the action of alcoholic potash, not yielding a trace of phenol or of chloride of potassium, even when heated with it for several hours. On the other hand, Church (Chem. Soc. J. xvi. 76), by heating benzene with hydrochloric acid and acid chromate of potassium, obtained a distillate containing, as chief product, the compound $C^{12}H^6Cl^2$ or $C^{12}H^5Cl.HCl$, which when heated with strong alcoholic potash yielded phenol; but as the chlorinated compound used in this experiment was the *crude* product of the action of nascent chlorine on benzene, which had not been submitted to any process of purification, it is by no means certain that the phenol thus obtained really resulted from the decomposition of phenylic chloride or chlorobenzene. The same crude distillate washed with aqueous potash and rectified, yielded phenylic chloride, which when distilled over sodium-amalgam left a residue containing phenyl, $C^{12}H^{10}$ (p. 409), together with a small quantity of a yellow crystalline body, probably chrysene, $nC^6H^4$, while the distillate contained, together with unaltered benzene, a hydrocarbon boiling at 91°, and likewise having the composition $C^6H^4$. (Church.)

Pure chlorobenzene is not attacked by acetate of silver, by an alcoholic solution of potassic acetate, or by ammonia. Heated with *sodium* it yields benzene (Riche), probably arising from a trace of moisture (see page 409).

**Dichlorobenzene,** $C^6H^4Cl^2$, is obtained by heating the chloroplatinate of azochlorophenylamine, $2(C^6H^3ClN^2.HCl).PtCl^4$, with carbonate of sodium, and crystallises in long needles or elongated four-sided plates, having the same peculiar aromatic odour as dibromobenzene. (Griess, Phil. Trans., 1864, [3], 705.)

**Trichlorobenzene,** $C^6H^3Cl^3$, has been already described (i. 543).

*Hydrochlorate of trichlorobenzene*, $C^6H^6Cl^6 = C^6H^3Cl^3.3HCl$, heated with acetate of silver, yields compounds resembling the glucosides in their power of reducing cupric oxide in alkaline solution. (Rosenstiehl, Jahresb. 1862, p. 481.)

**Chlorobromobenzene,** $C^6H^4ClBr$, is obtained by heating the chloroplatinate of azobromohenylmine with carbonate of sodium:

$$2(C^6H^3BrN^2.HCl)PtCl^4 \quad = \quad 2C^6H^4ClBr \quad + \quad Pt \quad + \quad Cl^4 \quad + \quad N^4.$$

The crystals which condense in the neck of the retort may be purified by pressing them between filter-paper, distilling a second time, and recrystallising from alcohol.

Chlorobromobenzene dissolves rather slowly in alcohol, but easily in ether, and crystallises from a hot saturated alcoholic solution on cooling, or from the ethereal solution by evaporation, in white needles or plates having a peculiar odour like that of benzene. (Griess, Phil. Trans. 1864, [3], 702.)

### *Iodobenzenes.*

**Monoiodobenzene** or **Iodide of Phenyl.**—Scrugham, by treating phenol with iodine and phosphorus, obtained a liquid which, after treatment with potash and rectification, boiled at 260°, and was found to contain iodine. This liquid was presumed to be iodide of phenyl, but the quantity obtained was not sufficient for a satisfactory investigation (Chem. Soc. J. xiii. 244). Several other chemists have attempted the preparation of phenylic iodide, with no better success.

**Bromiodobenzene**, $C^6H^4BrI$, formed by boiling the perbromide of azoiodophenylammonium (perbromide of diazoiodobenzene) $C^6H^4IN^2.Br^3$, with alcohol, crystallises from ether or alcohol in large white plates which are volatile without decomposition. (Griess.)

### *Nitrobenzenes.*

**Mono-** and **Di-nitrobenzene** have been already described (i. 543; iv. 59). The former is converted by *sodium-amalgam* into azobenzene (i. 477):

$$\underset{\text{Nitrobenzene.}}{2C^6H^5(NO^2)} + H^8 = \underset{\text{Azobenzene.}}{C^{12}H^{10}N^2} + 4H^2O.$$

Part of the azobenzene, however, takes up 2 at. hydrogen more, and is converted into benzidine. (Werigo, Ann. Ch. Pharm. cxxxv. 176.)

**Nitrobromobenzene,** $C^6H^4(NO^2)Br$, is produced by the action of fuming nitric acid on monobromobenzene (Couper, see i. 543). When treated with reducing agents it yields bromaniline, $C^6H^6BrN$. A nitro-bromobenzene having exactly the same composition and properties, is produced by heating bromoplatinate of β azonitrophenylamine (obtained from β nitraniline)* with carbonate of sodium:

$$2(C^6H^4(NO^2)N^2.HBr)Pt^{iv}Br^4 = 2C^6H^4(NO^2)Br + N^4 + Pt + Br^4;$$

or by heating the perbromide of β azonitrophenylammonium with alcohol;

$$C^6H^4(NO^2)N^2Br^3 = C^6H^4(NO^2)Br + N^2 + Br^2.$$

It melts at 126°† and crystallises in long white needles (Griess, Phil. Trans. 1864, [3], 712). An isomeric compound distinguished as α nitrobromobenzene is obtained in like manner from the perbromide of α azonitrophenylammonium. It crystallises in rhombic prisms which melt at 56° (Griess). α and β nitrobromobenzene treated with sulphide of ammonium, yield respectively α and β bromaniline. (Griess.)

**Nitrodibromobenzene,** $C^6H^3(NO^2)Br^2$, is obtained by the action of fuming nitric acid on dibromobenzene. When heated with alcoholic sulphide of ammonium it yields dibromaniline. (Riche and Bérard, Ann. Ch. Pharm. cxxxiii. 51.)

**Nitrotetrabromobenzene,** $C^6H(NO^2)Br^4$, is a crystalline product obtained by the action of fuming nitric acid on tetrabromobenzene. (Riche and Bérard.)

**Nitrochlorobenzene,** $C^6H^4(NO^2)Cl$, produced by boiling monochlorobenzene with strong nitric acid, crystallises in long needles, melts at 78° and solidifies at 74°. It dissolves sparingly in *water*, easily in hot *alcohol* and in *ether*. By *sulphide of ammonium* and other reducing agents it is converted into chloraniline. (Riche, Ann. Ch. Pharm. cxxi. 357.)

**Dinitrodichlorobenzene,** $C^6H^3(NO^2)^2Cl$, is formed by the action of pentachloride of phosphorus on dinitrophenic acid, perhaps thus:

$$\left.\begin{matrix}C^6H^3(NO^2)^2\\H\end{matrix}\right\}O + PCl^5 = C^6H^3(NO^2)^2Cl + PCl^3O + HCl.$$

The resulting yellowish liquid, decanted on cooling from the excess of chloride of phosphorus, solidifies in a few days to a crystalline mass which may be washed with cold and dissolved in hot alcohol. The alcoholic solution becomes milky on cooling, and deposits the compound as a yellow powder, which after a few days solidifies in needles. (Laurent and Gerhardt, Ann. Ch. Pharm. lxxv. 79.)

**Trinitrochlorobenzene, Trinitrophenylic chloride,** or **Chloropicryl,** $C^6H^2(NO^2)^3Cl$.—This compound is obtained by the action of 1 at. pentachloride of phosphorus on 1 at. picric acid:

$$C^6H^3(NO^2)^3O + PCl^5 = C^6H^2(NO^2)^3Cl + PCl^3O + HCl.$$

The two bodies act violently on each other at first, and copious fumes of hydrochloric acid are evolved. As soon as this action ceases, and oxychloride of phosphorus begins to pass over, the retort must be removed from the fire, because the chloropicryl would be decomposed by further heating, and a resinous substance formed: hence the chloropicryl cannot be completely purified from oxychloride of phosphorus by distillation. It is a yellow, solid body having an agreeable odour. Water decomposes it, forming hydrochloric and picric acids. It dissolves in alcohol and in ether. Carbonate of ammonium converts it into picramide (*q. v.*). (Pisani, Ann. Ch. Pharm. xcii. 326.)

**PHENYL, IODIDE OF.** See IODOBENZENE, p. 415.

**PHENYL, OXIDE OF.** $(C^6H^5)^2O$.—This compound appears to be formed by heating chloride of phenyl with phenate of sodium: $C^6H^5Cl + C^6H^5NaO = NaCl$

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* α nitraniline is the base produced by the action of sulphide of ammonium on dinitrobenzene; β nitraniline is the isomeric compound obtained by distilling certain nitrated phenylamides with potash (see PHENYLAMINES). This is the mode of distinction proposed by Hofmann, and generally adopted. In Griess's paper, however, above referred to, the meaning of the prefixes α and β is reversed.

† According to Couper, nitrobromobenzene prepared by the action of nitric acid on benzene, melts below 90°; but Griess has shown that the product thus obtained melts at exactly the same point as that prepared from the platinum-salt of α azonitrophenylamine.

+ $(C^6H^5)^2O$: the formation of chloride of sodium was observed, but no distillate was obtained (**Scrugham**). **List** and **Limpricht** (Ann. Ch. Pharm. xc. 209), by subjecting benzoate of copper to dry distillation, obtained, amongst other products, a colourless oil, boiling at 260°, and yielding by analysis 84·35—84·60 per cent. carbon and 5·99 hydrogen, numbers agreeing nearly with the composition of phenylic oxide, which requires 84·70 per cent. carbon, 5·88 hydrogen, and 10·42 oxygen.* This oil had an agreeable odour of geraniums, was insoluble in water, sparingly soluble in alcohol, very soluble in ether. It was not decomposed by alcoholic potash, but when heated with strong sulphuric acid it yielded a white crystalline body having very nearly the composition of phenyl, $C^{12}H^{10}$ (p. 409).

**PHENYL, SULPHIDES OF.** *Protosulphide*, $C^{12}H^{10}S$. (**Stenhouse**, Proc. Roy. Soc. xiv. 351.)—This compound, or a body isomeric with it, is obtained by the dry distillation of sulphobenzolate of sodium, $C^6H^5NaSO^3$. When this salt, in the form of dry powder and in quantity not exceeding 25—30 grammes, was heated in a copper flask, an oily body covered with a layer of water condensed in the receiver, and a considerable quantity of carbonic and sulphurous anhydrides was evolved, while carbonaceous matter and carbonate of sodium remained behind. The crude oil began to boil at about 80°, between which temperature and 110°, water and benzene passed over. The boiling point then rose quickly to 290°, at which temperature the greater portion of the liquid distilled over, leaving a black tarry residue; and this when more strongly heated gave a further quantity of an oily body which, when rectified, yielded the substance boiling at about 293°, and above 300° a liquid which after standing for some weeks deposited a few crystals.

The oil boiling between 290° and 300°, which amounted to about two-thirds the weight of the crude oil, yielded on rectification an oil boiling very constantly at 292·5°, and containing, after further rectification in a current of hydrogen, 77·12 per cent. carbon, 5·38 hydrogen, and 17·49 sulphur (mean), agreeing nearly with the formula $C^{12}H^{10}S$, which requires 77·41 C, 5·38 H, and 17·20 S.

Sulphide of phenyl is nearly colourless, with only a very faint yellow tinge, and has an aromatic but slightly alliaceous odour. It has a high refractive power, specific gravity 1·09, and boils at 292·5°. It is insoluble in *water*, very soluble in hot *spirit*, from which it partially separates on cooling, and is miscible in all proportions with *ether*, *benzene*, and *sulphide of carbon*. Its alcoholic solution mixed with *platinic chloride* gives a slight flocculent precipitate, which on standing resolves itself into a reddish-coloured oil. *Nitrate of silver* and *mercuric chloride* give no precipitate. It dissolves sparingly in cold strong *sulphuric acid*, forming a red solution; but on raising the temperature the whole dissolves, forming a greenish-black liquid, which becomes colourless when largely diluted with water, and on neutralisation with chalk yields an organic calcium-salt. The solution of the oil in strong sulphuric acid blackens and gives off sulphurous anhydride when very strongly heated. It is not acted upon by solutions of the alkalis, either aqueous or alcoholic, but is decomposed by heating with solid potash.

Sulphide of phenyl heated with strong *nitric acid*, or with *acid chromate of potassium* and dilute *sulphuric acid*, is converted into a crystalline substance having the composition of **Mitscherlich's** sulphobenzene, $C^{12}H^{10}SO^2$, but differing from it greatly both in chemical and in physical properties: hence for distinction called **sulphobenzolene** (*q. v.*).

*Disulphide*, $C^{12}H^{10}S^2$. (**C. Vogt**, Ann. Ch. Pharm. cxix. 142.)—This compound is produced from phenylic sulphydrate or phenyl-mercaptan: 1. By oxidation with nitric acid:

$$2(C^6H^5)HS + HNO^3 = (C^6H^5)^2S^2 + NO^2 + H^2O.$$

When phenyl-mercaptan is gently heated with nitric acid of specific gravity 1·2 in a retort connected with the beak of a Liebig's condenser till red fumes begin to escape, the action goes on of itself without further heating, and at its termination, the oil, which at first floats on the top of the liquid, sinks to the bottom, and solidifies on cooling to a crystalline mass which, when washed with water and dissolved in boiling alcohol, yields by spontaneous evaporation needle-shaped crystals of disulphide of phenyl.—2. A solution of phenylic mercaptan in alcoholic ammonia, left to evaporate spontaneously at ordinary temperatures in a wide cylindrical vessel half filled with it, also yields crystals of the disulphide.—3. A small quantity of this compound is obtained in the preparation of phenyl-mercaptan.

Disulphide of phenyl is obtained by the first method in long white shining needles; by the second in beautiful regularly developed crystals half an inch long, and having the form of orthorhombic prisms with truncation of the macrodiagonal and brachydiagonal lateral edges, and terminated by a simple dome. It has a faint not unpleasant odour, is insoluble in *water*, but easily soluble in *alcohol* and *ether;* melts at 60° to a yellowish oil, which when left at rest sometimes does not solidify till cooled to 25°. Though but slightly volatile, it distils without decomposition at a somewhat high temperature. *Nascent hydrogen* evolved by zinc and hydrochloric acid, converts it into phenyl-mercaptan. By the prolonged action of *nitric acid* it is converted into phenylsulphurous acid, $C^7H^6SO^3$.

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* List and Limpricht assigned to it the formula $C^{22}H^{18}O^2$, which requires 84·07 C and 5·73 H.

**PHENYL, SULPHYDRATE OF.** $C^6H^6S = \left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}S.$ *Phenyl-mercaptan* (Vogt, *loc. cit.*); *Benzylic Sulphydrate*, or *Benzylic Mercaptan* (Kolbe).—Produced by the action of nascent hydrogen on sulphophenylic chloride:

$$C^6H^5SO^2Cl + H^6 = C^6H^6S + HCl + 2H^2O.$$

It is prepared by pouring dilute sulphuric acid upon zinc in a capacious flask, and adding sulphophenylic chloride as soon as the evolution of hydrogen becomes rapid, taking care that the zinc projects considerably above the oily liquid at the botton. On distilling the liquid after twenty-four hours, the phenylic sulphydrate passes over with the aqueous vapour, and collects as an oil in the receiver. The residual saline solution contains a small quantity of phenylic disulphide. When large quantities of material are operated on, it is best to subject the oil to a second treatment with zinc and sulphuric acid.

Phenylic sulphydrate is a colourless, mobile, strongly refracting, oily liquid, having an intensely disagreeable odour. Specific gravity 1·078 at 14°. Boiling point about 165°. It burns with a bright white flame. When placed on the skin it produces a burning pain; its vapour attacks the eyes and produces giddiness. It is not miscible with *water*, but nevertheless imparts its odour thereto; it dissolves easily in *alcohol*, *ether*, *benzene* and *sulphide of carbon*. It dissolves *sulphur* with yellowish, and *iodine* with red-brown colour.

*Phenyl-sulphides* or *Phenyl-mercaptides.*—Phenylic sulphydrate, like the corresponding ethylic compound (ii. 547), is capable of exchanging its typic hydrogen for metals.

The *cupric salt*, $C^{12}H^{10}Cu''S^2$, is precipitated as a pale yellow powder on mixing the alcoholic solutions of phenylic sulphydrate and cupric acetate. The *lead-salt*, $C^{12}H^{10}Pb''S^2$, obtained in like manner, is a yellow crystalline body, which has a silky lustre when dry, becomes cinnabar-red at 120°, yellow again at 200°, melts above 230° to a red liquid, and solidifies again to a yellow mass on cooling.

*Mercury-salt*, $C^{12}H^{10}Hg''S^2$.—Phenyl-mercaptan acts very violently on mercuric oxide; when a drop of it is let fall on the dry oxide, great heat is produced and the whole mass is scattered about, and even the dilute alcoholic solution becomes very hot in contact with mercuric oxide. The mercuric phenylsulphide produced by this reaction crystallises from alcohol in white capillary needles, having a silky lustre when dry. On mixing the alcoholic solutions of mercuric chloride and phenyl-mercaptan, the double salt, $C^{12}H^{10}Hg''S.Hg''Cl^2$, is produced, and crystallises from a boiling alcoholic solution on cooling in white laminæ.

*Phenyl-sulphide of Silver*, $C^6H^5AgS$, is precipitated as a pale yellow crystalline powder on mixing the alcoholic solutions of phenyl-mercaptan and nitrate of silver. *Auric* and *platinic chlorides* form brown precipitates.

The *sodium-salt*, $C^6H^5NaS$, is formed, with evolution of hydrogen, on adding sodium to phenyl-mercaptan, and remains as a white saline mass on expelling the excess of the mercaptan. Carbonic anhydride passed into the alcoholic solution of this salt forms the compound $C^7H^5NaO^2S$, just as salicylate of sodium, $C^7H^5NaO^3$, is formed from phenate of sodium, $C^6H^5NaO$.

**PHENYL-ACETAMIDE** or *Acetanilide*, $C^8H^9NO = (C^6H^5)(C^2H^3O)HN$. (Gerhardt, Ann. Ch. Pharm. lxxxvii. 164.)—Produced by the action of aniline upon acetic anhydride or chloride of acetyl:

$$\begin{array}{lcccccccc} C^4H^6O^3 & + & C^6H^7N & = & C^8H^9NO & + & 2H^2O. \\ C^2H^3OCl & + & C^6H^7N & = & C^8H^9NO & + & HCl. \end{array}$$

It crystallises in colourless shining laminæ, melts at 112°, and solidifies in a crystalline mass on cooling; distils without decomposition. Sparingly soluble in cold, moderately soluble in hot water, also in alcohol and ether. Is scarcely acted upon by boiling potash-ley, but fused hydrate of potassium decomposes it immediately, forming aniline and acetate of potassium.

Phenylacetamide treated with *bromine* yields mono- and di-bromophenylacetamide according to the proportions used; similarly with *chlorine* (Mills, Proc. Roy. Soc. x. 589.—Griess, Ann. Ch. Pharm. cxxi. 257). With *fuming nitric acid* it yields nitrophenylacetamide. (Hofmann, Proc. Roy. Soc. x. 589.)

**PHENYLAMIC ACIDS.** *Anilic acids.*—Amic acids in which the hydrogen is more or less replaced by phenyl, and containing the elements of aniline and a polybasic acid *minus* the elements of water: *e. g.*

$$\left.\begin{matrix}\mathrm{H.C^6H^5}\\ \mathrm{(C^4H^4O^2)''}\\ \mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\ \mathrm{O}\end{matrix} \quad = \quad \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N} \quad + \quad \left.\begin{matrix}\mathrm{C^4H^4O^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2} \quad - \quad \mathrm{H^2O}.$$

Phenysuccinamic acid. Aniline. Succinic acid.

$$\left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{(C^6H^5O^4)'''}\\ \mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\ \mathrm{O}\end{matrix} \quad = \quad \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N} \quad + \quad \left.\begin{matrix}\mathrm{(C^6H^5O^4)'''}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{O^3} \quad - \quad \mathrm{2H^2O}.$$

Phenylcitramic acid. Aniline. Citric acid.

$$\left.\begin{matrix}\mathrm{H^2.(C^6H^5)^2}\\ \mathrm{(C^6H^5O^4)'''}\\ \mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\ \mathrm{O}\end{matrix} \quad = \quad 2\left(\left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right) \quad + \quad \left.\begin{matrix}\mathrm{(C^6H^5O^4)'''}\\ \mathrm{H^3}\end{matrix}\right\} \quad - \quad \mathrm{2H^2O}.$$

Diphenylcitramic acid.

They are produced either by direct elimination of water from salts of aniline, or by heating aniline with excess of the corresponding acids, or by heating the corresponding phenylimides with aqueous ammonia (see Amic Acids, i. 167). The individual phenylamic acids are described in connection with the corresponding primary amic acids (see Carbamic Acid, i. 751; Citric Acid, Amides of, i. 1000; Oxamic Acid, iv. 281).

**PHENYLAMIDES** or **ANILIDES.** Amides in which ⅓ of the hydrogen is replaced by phenyl. They contain the elements of neutral salts of aniline *minus* 1, 2, or 3 at. water, according as the acid is monobasic, dibasic or tribasic: *e. g.*

$$\left.\begin{matrix}\mathrm{C^7H^5O}\\ \mathrm{C^6H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N} \quad = \quad \mathrm{C^7H^6O^2.C^6H^7N} \quad - \quad \mathrm{H^2\Theta}.$$

Phenyl-benzamide. Benzoate of aniline.

$$\left.\begin{matrix}\mathrm{(C^4H^4O^2)''}\\ \mathrm{(C^6H^5)^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N^2} \quad = \quad \mathrm{C^4H^6O^4.2C^6H^7N} \quad - \quad \mathrm{2H^2\Theta}.$$

Phenyl-succinamide. Succinate of aniline.

$$\left.\begin{matrix}\mathrm{(C^6H^5O^4)'''}\\ \mathrm{(C^6H^5)^3}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{N^3} \quad = \quad \mathrm{C^6H^8O^7.3C^6H^7N} \quad - \quad \mathrm{3H^2\Theta}.$$

Citrate of aniline.

Phenyl-citramide.

They are formed by dry distillation of the aniline-salts, or by the action of acid anhydrides, or chlorides of acid-radicles, on aniline.

Phenylimides or Anils.—Tertiary monamides in which 2 at. H are replaced by a diatomic acid-radicle, and the remaining atom by phenyl. They are produced from acid salts of aniline by elimination of 2 at. water, and may be regarded as aniline, in which 2 at. H are replaced by a diatomic radicle: *e. g.*

$$\left.\begin{matrix}\mathrm{(C^4H^4O^2)''}\\ \mathrm{C^6H^5}\end{matrix}\right\}\mathrm{N} \quad = \quad \mathrm{C^4H^6O^4.C^6H^7N} \quad - \quad \mathrm{2H^2O}.$$

Phenyl-succinimide. Acid succinate of aniline.

Heated with aqueous ammonia, they take up 1 at. water and are converted into the corresponding phenylamic acids: *e. g.*

$$\mathrm{C^{10}H^9NO^2} \quad + \quad \mathrm{H^2O} \quad = \quad \mathrm{C^{10}H^{11}NO^3}.$$

Phenyl-succinimide. Phenyl-succinamic acid.

**PHENYLAMINES.** Organic bases derived from ammonia by the substitution of one or more atoms of phenyl for an equivalent quantity of hydrogen.

### A. Phenyl-monamines.

**Monophenylamine** or **Aniline.** $\mathrm{C^6H^7N} = \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N}$. *Crystalline, Kyanol, Benzidam, Phenamide, Amidophénase.*—Regarded by Griess as *amido-benzene*, $\mathrm{C^6H^5(NH^2)}$, by L. Gmelin as $\mathrm{C^6H^5N.H^2}$. (Undverdorben, Pogg. Ann. viii. 397.—Runge, *ibid.* xxxi. 65, 513; xxxii. 331.—Fritzsche, J. pr. Chem. xx. 453; xxvii. 153; xxviii. 202.—Zinin, *ibid.* xxvii. 149; xxxvi. 98.—Hofmann, Ann. Ch. Pharm. xlvii. 31; liii. 8; lvii. 265; lxvi. 129; lxvii. 61, 129; lxx. 129; lxxiv. 117; lxxv. 356.—*Report on Chemical Products and Processes in the International Exhibition of* 1862, p. 123.—

Muspratt and Hofmann, Ann. Ch. Pharm. liii. 221; lvii. 210.—Laurent, Compt. rend. xvii. 1366; Rev. scient. xviii. 278, 280.—Gerhardt, J. Pharm. [3] ix. 401; x. 5.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 163.—Gm. xi. 246.—Gerh. iii. 79.)

*History.*—Aniline was discovered in 1826 by Unverdorben, who obtained it from indigo and called it *crystalline*, on account of the facility with which its salts assume the crystalline form: the name *aniline* is derived from *anil*, a Portuguese name of the indigo plant. Aniline has been especially studied by Hofmann, Fritzsche, Zinin, and Gerhardt, who have obtained from it a large number of compounds and derivatives. For some time, however, it remained an object of purely scientific interest, and was not applied to any technical purpose; but within the last ten years it has acquired great industrial importance, and is now manufactured in enormous quantities, on account of the splendid dyes which it is capable of yielding.

*Formation.*—Aniline is produced in a great number of reactions: 1. By heating phenol with ammonia in a sealed tube for a fortnight or three weeks (Laurent):

$$C^6H^6O \quad + \quad NH^3 \quad = \quad C^6H^7N \quad + \quad H^2O.$$

2. From nitrobenzene by the reducing action: α. Of sulphydric acid in presence of alcohol and ammonia (Zinin):

$$C^6H^5NO^2 \quad + \quad 3H^2S \quad = \quad C^6H^7N \quad + \quad 2H^2O \quad + \quad S^3;$$

β. Of zinc, in presence of hydrochloric acid (Hofmann):

$$C^6H^5NO^2 \quad + \quad H^6 \quad = \quad C^6H^7N \quad + \quad 2H^2O;$$

γ. Of ferrous acetate:

$$C^6H^5NO^2 \quad + \quad 6FeO \quad + \quad H^2O \quad = \quad C^6H^7N \quad + \quad 3Fe^2O^3;$$

ferrous sulphate, oxalate, and chloride do not exert any reducing action on nitrobenzene (Béchamp, Ann. Ch. Phys. [3] xlii. 186).—δ. Of a hot solution of arsenious acid in caustic soda (Wöhler, Ann. Ch. Pharm. cii. 127):

$$2C^6H^5NO^2 \quad + \quad 3As^2O^3 \quad + \quad 2H^2O \quad = \quad 2C^6H^7N \quad + \quad 3As^2O^5;$$

ε. Together with azobenzene and oxalic acid, by distilling nitrobenzene with alcoholic potash:

$$2C^6H^5NO^2 + C^2H^6O + 2KHO = C^6H^7N + C^6H^5N + C^2K^2O^4 + 2H^2O;$$

ζ. According to Letheby (Chem. Soc. J. xvi. 161) nitrobenzene is converted into aniline in the stomach.

3. By the dry distillation of the isomeric compounds phenyl-carbamic acid (Fritzsche), salicylamide and nitrotoluene (hydride of nitrobenzoyl) (Hofmann and Muspratt):

$$C^7H^7NO^2 \quad = \quad C^6H^7N + CO^2.$$

4. By the action of phosphoric anhydride, chloride of zinc, or hydrochloric acid on diphenylcarbamide and diphenyl-sulphocarbamide (Hofmann, Proc. Roy. Soc. ix. 274):

$$\begin{array}{cccccc} C^{13}H^{12}N^2O & = & C^6H^7N & + & C^7H^5NO. \\ \text{Diphenyl-carbamide.} & & \text{Aniline.} & & \text{Phenylic cyanate.} \\ C^{13}H^{12}N^2S & = & C^6H^7N & + & C^7H^5NS. \\ \text{Diphenyl-sulphocarbamide.} & & \text{Aniline.} & & \text{Phenylic sulphocyanate.} \end{array}$$

5. By the distillation of azoxybenzene. (Zinin, i. 479.)

6. By distilling indigo *per se* (Unverdorben), or with very strong aqueous potash (Fritzsche); also, by distilling isatin with potash (Hofmann):

$$\begin{array}{cccccccccccc} C^8H^5NO & + & 4KHO & + & H^2O & = & C^6H^7N & + & 2K^2CO^3 & + & H^4. \\ \text{Indigo.} \\ C^8H^5NO^2 & + & 4KHO & & & = & C^6H^7N & + & 2K^2CO^3 & + & H^2. \\ \text{Isatin.} \end{array}$$

7. Aniline is found among the products of the distillation of coal (Runge); of peat (Vohl, J. Pharm. [3] xxxvi. 319); and of bones (Anderson).

According to Phipson, certain fungi of the genus *Boletus* (*B. cyanescens* and *B. luridus*), the tissue of which acquires a transient blue colour when triturated in contact with the air, contain aniline.

*Preparation.*—1. From *Nitrobenzene.*—Of the various modes of converting nitrobenzene into aniline, the reduction by ferrous acetate is the only one that is now used as a practical method of preparation. It is by this method indeed that the large quantities of aniline required for the production of aniline colours are prepared. The nitrobenzene is mixed with acetic acid in cast-iron vessels, and cast-iron turnings or filings are very gradually added, care being taken that the heat produced by the reaction does not rise too high. Equal weights of the three substances are very convenient proportions. The mixture is soon converted into a solid or semi-solid mass, consisting principally of ferrous acetate and acetate of aniline. This is distilled, either alone or with addition of lime, in large cast-iron cylinders, the mass being gradually raised to a red heat. The distillate may vary in composition, but it generally consists of acetone, aniline, unaltered nitrobenzene, and other products arising from the impurities of the nitrobenzene. If the iron and acetic acid are used in great excess, the decomposition, as observed by Scheurer-Kestner, may go too far, so as to reproduce benzene, with simultaneous evolution of ammonia:

$$3C^6H^7N + Fe^2 + 3H^2O = 3C^6H^6 + 3NH^3 + Fe^2O^3.$$

The crude aniline mixture is redistilled, and the aniline obtained sufficiently pure for manufacturing purposes, by collecting the portions distilling between 175° and 190°. It may be further purified by distillation with potash, and subsequent rectification.

According to A. Kremer (J. pr. Chem. xc. 255), nitrobenzene may be advantageously converted into aniline by means of zinc-dust and water, without the aid of an acid:

$$C^6H^5(NO^2) + Zn^3 + H^2O = C^6H^7N + 3Zn''O.$$

From 2 to 2½ pts. of zinc-dust (the product containing from 80 to 95 per cent. of the metal which passes over it in the reduction of zinc-ore at the commencement of the distillation), are heated with 5 pts. water and 1 pt. nitrobenzene in a retort with a condensing tube directed upwards, a gentle heat being applied at first, and afterwards raised to the boiling point. When the transformation is complete (which may be known by the perfect solubility of the product in dilute hydrochloric acid), the aniline (amounting to 63—65 per cent. of the nitrobenzene) is distilled off with water. The reduction may also be effected, though much more slowly, by iron reduced with hydrogen.

2. From *Coal-tar.*—Aniline exists ready formed in coal-tar oil, but mostly in small quantity, not exceeding 1 per cent., so that its separation cannot be advantageously performed, excepting when very large quantities (from 1000 to 2000 lbs.) are to be operated on. The coal-tar oil is shaken up in carboys with strong hydrochloric acid; and the watery layer below the oil is removed with a syphon, filtered through coarse paper and distilled with excess of slaked lime in a copper still. The distillate thus obtained is a mixture of ammonia, pyridine, picoline, aniline, leucoline (coal-tar chinoline, iii. 583) and other bases nearly allied to the last, the three first mentioned bases, or the others, predominating according as a more or less volatile coal-tar oil has been used. The so-called "dead oil" which sinks in water (i. 1038) yields when thus treated scarcely anything but aniline and leucoline bases; and from this mixture the aniline may be separated by the process described under CHINOLINE (i. 870).

3. From *Indigo.*—Pulverised indigo is introduced into very strong aqueous potash contained in a retort; the resulting brown mass is heated as long as ammoniacal water and a brown oil pass over with intumescence; and the oil is separated by distillation into a brown resinous residue, and a colourless distillate of aniline, amounting to 20 per cent. of the indigo. (Fritzsche.)

*Properties.*—Aniline is a transparent, colourless, mobile, oily liquid, having a faint vinous, not unpleasant odour, and an aromatic burning taste. It retains its mobility at 20°, but solidifies at the temperature of a mixture of ether and solid carbonic acid. It boils at 182° (Hofmann). Specific gravity = 1·020 at 16° (Hofmann), 1·028 (Fritzsche). Vapour-density, obs. = 3·210; calc. (2 vol.) = 3·234. Index of refraction = 1·577 (Hofmann). It is a non-conductor of electricity. Its vapour burns with a bright but smoky flame. It exerts a deleterious action on the animal organism: half a gramme mixed with 1½ grm. of water and sprinkled into the mouth of a rabbit, produced strong cramps, then laborious breathing, loss of strength, dilated pupils, and inflammation of the mucous membrane of the mouth; when dropt into the eye, it does not dilate the pupil (Hofmann). According to Schuchardt (Jahresb. 1861, p. 495), frogs immersed in water containing 1 pt. in 8000 of aniline, die in two or three hours. Eight drops killed a frog in a quarter of an hour, and three drops applied to a wound in the back, caused death in two hours. A dose of 50 to 100 drops killed rabbits in four to six hours. According to Wöhler and Frerichs (Ann. Ch. Pharm. lxv. 343), aniline does not exert any poisonous action upon dogs. The aqueous solution kills leeches, and parts of plants immersed in it. (Runge.)

Aniline dissolves in all proportions in *ether, alcohol, wood-spirit, acetone, sulphide of carbon* and *oils,* both fixed and volatile. It is slightly soluble in *water,* and likewise takes up a small quantity of that liquid. The aqueous solution has an extremely weak alkaline reaction, affecting only the most delicate test-papers; it does not blue reddened litmus or redden turmeric, but it changes the violet colour of dahlias to green. Aniline dissolves *sulphur* abundantly; also *phosphorus*, *camphor* and *colophony*, but not arsenic, copal or caoutchouc. It produces a bright violet-blue colour with *chloride of lime* and other *hypochlorites*, blue with *sulphuric acid and acid chromate of potassium*, and reds of various depth and brightness when heated with *tetrachloride of carbon*, *stannic chloride*, *arsenic acid*, *fuming nitric acid*, *mercuric nitrate*, and some other salts. It imparts a deep yellow colour to *pine-wood* and *elder pith*, a character however likewise exhibited, though in a less degree, by other bases, namely conine, cinnamine, leucoline and naphthylamine.

The aqueous solution of aniline precipitates the bases from ferrous, ferric, zinc, and aluminium salts. With platinic and palladious chlorides it forms yellow double salts; with chloride of gold a red-brown double salt; with mercuric, antimonic and stannic chlorides, white double salts. It forms with infusion of galls a brownish-yellow flocculent precipitate, soluble in alcohol and in hot water, and coagulates albumin.

*Decompositions.*—1. When aniline-vapour is passed through a red-hot glass tube, charcoal is deposited, ammonia and hydrocyanic acid are given off, and a brown liquid condenses in the receiver, which, after the undecomposed aniline has been saturated with an acid, yields by distillation, benzene boiling at 80°, and benzonitrile (cyanide of phenyl) boiling at 190°—195°. The formation of the latter is probably due to the action of the hydrocyanic acid on another portion of the aniline, $C^6H^7N + CNH = C^7H^5N + NH^3$. A small quantity of an indifferent crystalline substance, and an oily base of high boiling point are likewise found among the products of the decomposition. (Hofmann, Proc. Roy. Soc. xii. 383.)

2. When exposed to the *air*, it turns yellow, red and brown, and forms a resin which dissolves with yellow colour in water, the change taking place more quickly as the temperature is higher: hence in distilling aniline it is necessary either to use a brisk fire, or to pass a stream of hydrogen or carbonic anhydride through the apparatus.

3. Aniline treated with dilute *sulphuric acid* and *peroxide of manganese*, yields a small quantity of quinone together with ammonia:

$$C^6H^7N + O^2 = C^6H^4O^2 + NH^3.$$

The greater part of the aniline appears however to undergo a further decomposition (Hofmann, Proc. Roy. Soc. xiii. 4). The formation of ammonia in this reaction was also observed by Matthiessen (*ibid.* ix. 637).

4. Aniline takes fire in contact with *chromic anhydride* ($CrO^3$), and burns with a bright flame and agreeable odour, leaving a residue of green chromic sesquioxide, $Cr^2O^3$. (Hofmann.)

5. An aqueous solution of *chromic acid* forms with aniline or its salts, a green, blue, or black precipitate, according to the concentration of the solution (Fritzsche). Aniline or an aniline-salt moistened on a porcelain dish with a few drops of *sulphuric acid* and solution of *potassic chromate*, produces a bright but transient blue coloration (Beissenhirtz, Ann. Ch. Pharm. lxxxvii. 376). On this reaction is founded the preparation of mauve, or aniline-violet discovered by Perkin (see Appendix to this article).

6. With solutions of *alkaline hypochlorites*, chloride of lime, for example, aniline exhibits a deep violet-purple coloration gradually passing into dingy red (Runge). This reaction affords a very delicate test for aniline; it is likewise exhibited, though still more transiently, by aniline-salts. The purple colour is not altered by alkalis; acids change it to red.

7. A solution of aniline in dilute sulphuric acid is easily decomposed by the *electric current*; and if a drop of the solution be laid on a piece of platinum foil connected with the positive pole of a small Grove's battery (one pair is sufficient), and the negative terminal also dipped into it, the liquid immediately assumes a fine blue colour changing to violet and red, the colours being very bright in strong solutions, and affording a very delicate test for aniline. The colouring matter is ultimately deposited on the platinum foil as a blackish-brown powder, insoluble in water, alcohol, ether, and ammonia, but soluble, with blue, green or violet colour, in strong sulphuric acid, whence it is precipitated by water as a dingy green powder; it is partially decolorised by reducing agents. (H. Lothoby, Chem. Soc. J. xvi. 161.)

8. Aniline treated with a mixture of *potassic chlorate* and *hydrochloric acid* forms a red resinous substance containing trichlorophenic acid and perchloroquinone, from which the former may be dissolved out by boiling alcohol.

9. Aniline is decomposed by *nitric acid*, and when evaporated at 100°, leaves a brown-black residue (Runge). It is immediately reddened by strong nitric acid (Zinin).

It acquires a transient blue and green colour by treatment with strong nitric acid (Fritzsche). With a small quantity of fuming nitric acid, it immediately forms a deep azure-blue mixture, which when very slightly warmed, turns yellow, becomes hot, gives off gas with violence, then assumes a scarlet colour continually increasing in brightness, and deposits picric acid (Hofmann). Aniline, dissolved in moderately strong nitric acid, likewise passes into spontaneous ebullition on the application of a gentle heat, gives off nitrous vapours, and when that action ceases, is found to be converted into picric acid (Hofmann and Muspratt):

$$C^6H^7N \quad + \quad 6NHO^3 \quad = \quad C^6H^3(NO^2)^3O \quad + \quad 4NHO^2 \quad + \quad 3H^2O.$$

Nitric acid heated with excess of aniline, or nitrate of aniline heated with aniline to 150°—160° for several hours, forms a beautiful violet-red substance, which is one of the varieties of aniline-red. A similar colouring matter is obtained by heating aniline with *mercuric* or *mercurous nitrate*, with *nitrate of lead, nitrate of silver, arsenic acid, stannic chloride, antimonic nitrate*, and a variety of other salts. All these red colours have been shown by Hofmann to consist of various salts of rosaniline, $C^{20}H^{19}N^3$ (see Appendix to this article).

10. *Nitrous acid* acts upon aniline in various ways according to the manner in which the two bodies are brought together: *a.* When hydrochlorate of aniline is treated with *nitrite of silver* or *nitrite of potassium*, nitrogen is evolved and phenol is formed, together with a metallic chloride and water (T. S. Hunt, Sill. Am. J. [2] viii. 372.—Hofmann, Chem. Soc. J. iii. 232):

$$C^6H^7N.HCl \quad + \quad AgNO^2 \quad = \quad C^6H^6O \quad + \quad AgCl \quad + \quad H^2O \quad + \quad N^2.$$

According to Hunt, phenol is likewise obtained when nitric oxide is passed into a dilute aqueous solution of nitrate of aniline:

$$C^6H^7N \quad + \quad HNO^2 \quad = \quad C^6H^6O \quad + \quad H^2O \quad + \quad N^2;$$

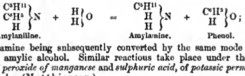
but according to Hofmann, the whole or the greater part of the phenol thus produced is converted into mononitrophenol by the free nitric acid present.

According to Matthiessen, however (Proc. Roy. Soc. ix. 118), the action takes place by two stages, the aniline in the first instance reacting merely with water, to produce ammonia and phenol:

$$C^6H^7N \quad + \quad H^2O \quad = \quad H^3N \quad + \quad C^6H^6O,$$

while in the second stage, the ammonia and nitrous acid act on one another so as to form water and free nitrogen: $H^3N + HNO^2 = 2H^2O + N^2$, and the phenol is converted by the free nitric acid into nitrophenol.

In like manner a solution of nitrate of amylaniline is converted by nitrous acid into amylamine and phenol, the action in this, as in the former case, consisting in a replacement of phenyl by hydrogen:



$$\underset{\text{Amylaniline.}}{\left.\begin{matrix}C^5H^{11}\\C^6H^5\\H\end{matrix}\right\}N} \quad + \quad \left.\begin{matrix}H\\H\end{matrix}\right\}O \quad = \quad \underset{\text{Amylamine.}}{\left.\begin{matrix}C^5H^{11}\\H\\H\end{matrix}\right\}N} \quad + \quad \underset{\text{Phenol.}}{\left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O};$$

and the amylamine being subsequently converted by the same mode of action into ammonia and amylic alcohol. Similar reactions take place under the influence of *nitric acid*, of *peroxide of manganese* and *sulphuric acid*, of *potassic permanganate*, and of *caustic potash*. (Matthiessen.)

*β.* Nitrous acid passed into an *alcoholic* solution of aniline converts it into azodiphenyldiamine, $C^{12}H^{11}N^3$, a base formed from a double molecule of aniline, $C^{12}H^{14}N^2$, by the substitution of 1 at. nitrogen for 3 at. hydrogen:

$$2C^6H^7N \quad + \quad HNO^2 \quad = \quad C^{12}H^{11}N^3 \quad + \quad 2H^2O.$$

Similar reactions take place with the bromo-, chloro- and nitro-phenylamines, and with all the homologues of aniline, the general equation for the reaction being:

$$2C^nH^{2n-5}N \quad + \quad HNO^2 \quad = \quad C^{2n}H^{4n-13}N^3 \quad + \quad 2H^2O$$

(Griess, Ann. Ch. Pharm. cxiii. 334; suppl. i. 100). When nitrous acid is passed into a mixture of aniline with about four times its volume of alcohol, the azodiphenyldiamine first produced is ultimately converted into azophenylamine (or diamidobenzene), $C^6H^4N^2 = (C^6H^4N''')N$:

$$C^{12}H^{11}N^3 \quad + \quad NHO^2 \quad = \quad 2C^6H^4N^2 \quad + \quad 2H^2O.$$

11. *Chlorine gas* passed through dry aniline, converts it, with great rise of temperature and evolution of hydrochloric acid, into a black viscid tar, which stops up the gas-delivery tube. If, in order to prevent this accident, the chlorine be passed through

aniline mixed with water, or dissolved in hydrochloric acid or in alcohol, the liquid, which assumes first a blue, then a black colour, deposits a black tar, which on cooling solidifies into a brittle resin; and this resin distilled with a small quantity of water, yields **trichloraniline**, afterwards liquefies, leaves a residue of charcoal, and gives off hydrochloric acid and **trichlorophenic acid** in the form of a yellow offensive oil which crystallises on cooling (**Hofmann**):

$$C^6H^7N + Cl^6 = \underset{\text{Trichloraniline.}}{C^6H^4Cl^3N} + 3HCl;$$

and:

$$C^6H^7N + Cl^6 + H^2O = \underset{\text{Trichlorophenic acid.}}{C^6H^3Cl^3O} + 2HCl + NH^4Cl.$$

Trichloraniline appears also to be formed when aniline is distilled with hydrochloric acid and peroxide of manganese. (**Hofmann.**)

12. *Bromine* forms with anhydrous aniline, with great evolution of heat, a brown solution, which, if the quantity of bromine is sufficient, solidifies to a mixture of finely crystalline **tribromaniline** and hydrobromic acid (**Fritzsche.**)—*Bromine-water* added to aniline dissolved in hydrochloric acid, forms a considerable quantity of hydrobromic acid, and a precipitate of **tribromaniline** which quickly becomes crystalline; the same substance is deposited, after boiling aniline with excess of hydrobromic acid, in the form of a dark coloured oil which crystallises on cooling (**Hofmann**).—13. The dark brown solution of *iodine* in aniline, the formation of which is attended with great rise of temperature, soon deposits long needles of **hydriodate of aniline** (**Fritzsche, Hofmann**), while the mother-liquor retains, together with a portion of this salt and free iodine, an ioduretted brown amorphous resin, together with **hydriodate of iodaniline**:

$$C^6H^7N + I^2 = C^6H^6IN.HI.$$

14. *Cyanogen* acts differently from chlorine, bromine and iodine, not removing a portion of the hydrogen and taking its place, but uniting directly with the aniline, and forming the compound $C^6H^7NCy = C^7H^7N^2$, called **cyananiline**, which is also basic and forms salts with acids.

15. The *bromides* and *iodides of the alcohol-radicles* heated with aniline give rise to substitution-products in which one or two of the typical hydrogen-atoms of the aniline are replaced by alcohol-radicles, *e. g.* **ethylaniline** $(C^6H^5)(C^2H^5)HN$, **diamylaniline** $(C^6H^5)(C^5H^{11})^2N$, **methyl-ethyl-aniline** $(C^6H^5)(CH^3)(C^2H^5)N$. These compounds are bases like aniline itself: those in which the whole of the hydrogen is replaced by alcohol-radicles unite with the alcoholic iodides, forming iodides of bases belonging to the ammonium-type; thus diethylaniline with iodide of ethyl forms the iodide of **triethyl-phenylammonium** $(C^6H^5)(C^2H^5)^3NI$. (**Hofmann.**)

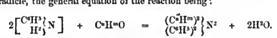
16. Aniline heated with *bromide of ethylene* yields, besides hydrobromate of aniline, the hydrobromates of three bases, having the same percentage composition $C^8H^9N.HBr$, and separable by their different degrees of solubility in alcohol, the first being soluble in cold alcohol; the second, which forms the chief part of the product, being insoluble in cold, but soluble in boiling alcohol; the third, insoluble in alcohol even at the boiling heat. Their formation is represented by the equation:

$$2C^6H^7N + C^2H^4Br^2 = C^8H^9N.HBr + C^6H^7N.HBr.$$

The second of these bases is shown, by its reactions with bromide of ethylene, iodide of methyl, &c., to consist of **diethylene-diphenyl-diamine**, $C^{16}H^{18}N^2 = \left.\begin{matrix}(C^2H^4)^2\\(C^6H^5)^2\end{matrix}\right\}N^2$; the first is probably **ethylene-phenylamine** $C^8H^9N$, and the third, **triethylene-triphenyl-triamine** $C^{24}H^{27}N^3$. Bromide of ethylene, heated with a large excess of aniline, forms **ethylene-diphenyl-diamine**, according to the equation $4C^6H^7N + C^2H^4Br^2 = \left.\begin{matrix}(C^2H^4)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2 + 2(C^6H^7N.HBr)$. (**Hofmann**, Proc. Roy. Soc. ix. 277; x. 104). The formation of a base having the composition $C^8H^9N$, by the action of chlorine on *chloride of ethylene*, had previously been observed by **Natanson** (Ann. Ch. Pharm. xcviii. 202).

17. *Aldehyde* (oxide of ethylidene, $C^2H^4O$) acts upon aniline in a similar manner, producing two compounds isomeric with the ethylene-bases just mentioned, but differing from them in properties, and related to them in the same manner as aldehyde to oxide of ethylene, that is to say, containing ethylidene instead of ethylene. With *valeraldehyde, œnanthol, benzoic aldehyde* (bitter almond oil) and other aldehydes, analogous reactions are produced, resulting, however, in each case, in the formation of only one

compound analogous to the preceding, namely a compound containing 2 at. of the aldehyde-radicle, the general equation of the reaction being:



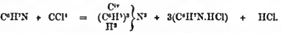
$$2\left[\left.\begin{matrix}C^6H^5\\H^2\end{matrix}\right\}N\right] + C^nH^mO = \left.\begin{matrix}(C^nH^m)^2\\(C^6H^5)^2\end{matrix}\right\}N^2 + 2H^2O.$$

With *acetones* or *ketones* no such reaction takes place (H. Schiff, Ann. Ch. Pharm. Suppl. iii. 342). See PHENYL-DIAMINES.

18. Aniline heated with an equal volume of *chloroform* to 180°—190° in a sealed tube, yields hydrochlorate of xylyl-diphenyl-diamine $\left.\begin{matrix}(CH)'''\\(C^6H^5)^2\\H\end{matrix}\right\}N^2$, together with hydrochlorate of aniline (Hofmann, *loc. cit.*):

$$4C^6H^7N + CHCl^3 = C^{19}H^{16}N^2.HCl + 2(C^6H^7N.HCl).$$

19. *Tetrachloride of carbon* heated with three times its volume of aniline for about thirty hours to 170°—180° yields a blackish mass partly soluble in water. From the aqueous solution, potash separates an oily precipitate which when distilled with potash gives off a considerable quantity of unaltered aniline, whilst a viscid oil remains behind and gradually solidifies to a crystalline mass, which when washed with cold alcohol and crystallised two or three times from boiling alcohol, yields a perfectly white crystalline body consisting of carbotriphenyltriamine $C^{19}H^{17}N^3$, whilst the alcohol retains in solution a substance of a magnificent crimson colour. The formation of carbotriphenyltriamine is represented by the equation:



$$6C^6H^7N + CCl^4 = \left.\begin{matrix}C^{iv}\\(C^6H^5)^3\\H^2\end{matrix}\right\}N^3 + 3(C^6H^7N.HCl) + HCl.$$

The portion of the black mass which is insoluble in water, dissolves almost entirely in dilute hydrochloric acid, from which it is precipitated by alkalis as an amorphous, pink or dingy precipitate soluble in alcohol with a rich crimson colour. The greater portion of this body consists of the same colouring principle which accompanies the white crystalline substance. (Hofmann, Proc. Roy. Soc. ix. 284.)

20. With *chloride of carbonyl* (phosgene gas) aniline yields a mixture of hydrochlorate of aniline and diphenylcarbamide, perhaps thus:

$$3C^6H^7N + COCl^2 = (CO)''(C^6H^5)^2H^2N^2 + C^6H^7N.HCl + HCl.$$

21. Dry gaseous *chloride of cyanogen* converts anhydrous aniline into melaniline; with an aqueous solution of the gas, aniline forms phenylcarbamide (Hofmann):

$$\underset{\text{Aniline.}}{2C^6H^7N} + CNCl = \underset{\text{Hydrochlorate of melaniline.}}{C^{13}H^{13}N^3.HCl.}$$

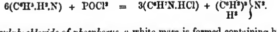
$$\underset{\text{Aniline.}}{2C^6H^7N} + CNCl + H^2O = \underset{\text{Phenyl-carbamide.}}{(CO)''(C^6H^5)H^3N^2} + \underset{\text{Hydrochlorate of aniline.}}{C^6H^7N.HCl.}$$

Dry chloride of cyanogen passed through an ethereal solution of aniline cooled with ice, forms cyanilide $C^6H^6CyN$, and hydrochlorate of aniline (Cahours and Cloez, Compt. rend. xxxviii. 354):

$$2C^6H^7N + CyCl = C^6H^6CyN + C^6H^7N.HCl.$$

22. *Bromide of cyanogen* acts upon aniline like volatile chloride of cyanogen, forming hydrobromate of melaniline, and [in presence of water?] a small quantity of phenyl-carbamide (Hofmann).—23. *Iodide of cyanogen* forms with aniline: iodaniline, a brown product containing iodine, and hydrocyanic acid (Hofmann).—24. When *persulphocyanic acid* (p. 374) is heated with anhydrous aniline, the mixture melts, and solidifies on cooling into a mass which dissolves in boiling alcohol and ether, and when boiled with water containing a little potash, leaves a residue of sulphur, and yields a filtrate from which hydrochloric acid precipitates, together with sulphur, crystalline scales which dissolve in boiling alcohol and ether. (Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 198.)

25. With *oxychloride of phosphorus*, anhydrous aniline forms triphenyl-phosphamide and hydrochlorate of aniline:



$$6(C^6H^5.H^2.N) + POCl^3 = 3(C^6H^7N.HCl) + \left.\begin{matrix}(PO)'''\\(C^6H^5)^3\\H^3\end{matrix}\right\}N^3.$$

With *sulphochloride of phosphorus*, a white mass is formed containing hydrochlorate of aniline and probably triphenyl-sulphophosphamide, $(PS)'''(C^6H^5)^3N^3H^3$. (Schiff, Ann. Ch. Pharm. ci. 299.)

26. *Chloride of benzoyl* converts aniline into a mixture of hydrochlorate of aniline and phenyl-benzamide, $(C^7H^5O)(C^6H^5)HN$. In like manner with the chlorides of *cumyl, cinnamyl,* and *anisyl,* aniline yields phenyl-cumylamide, phenyl-cinnamide, and phenyl-anisamide.

27. With *sulphophenylic chloride,* $C^6H^5SO^2Cl$, it forms phenyl-sulphophenylamine, $\left.\begin{matrix}C^6H^5\\ C^6H^5SO^2\\ H\end{matrix}\right\}N$, or thiophenylamic acid, $\left.\begin{matrix}(C^6H^5)^2\\ (SO)''\\ H\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix}$ (Chiozza and Biffi, *Gerhardt's Traité*, iii. 981):

$$C^6H^7N.C^6H^5SO^2Cl \quad = \quad C^{12}H^{11}NSO^2 \quad + \quad HCl.$$

28. Strong *sulphuric acid* converts aniline into phenyl-sulphamic acid, $C^6H^7NSO^3$, which when heated with excess of fuming sulphuric acid, yields phenyl-disulphamic acid, $C^6H^7NS^2O^6$ (Buckton and Hofmann, Chem. Soc. J. ix. 260). 26. With *phosphoric anhydride* it appears to form phenyl-phosphamic acid, $C^6H^8NPO^2 = \left.\begin{matrix}C^6H^5\\ (PO)'''\\ H\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix}$ (Ann. Ch. Pharm. ciii. 168). 27. Heated with various *organic acids,* it also forms the corresponding phenylamic acids (p. 419).

29. With *cyanic acid,* aniline forms phenyl-carbamide, $(CO)''(C^6H^5)H^3N^2$, or diphenyl-carbamide $(CO)''(C^6H^5)^2H^2N^2$, according to the circumstances of the reaction (i. 755).

30. With *sulphide of carbon* it forms phenyl-sulphocarbamide, $(CS)''(C^6H^5)^2H^2N^2$ (Hofmann, i. 756). The same compound is produced by distilling a mixture of aniline, sulphuric acid, and sulphocyanate of potassium. According to Crossley (Chem. News, iv. 196), a mixture of aniline and sulphide of carbon is converted in a few days, with evolution of sulphuretted hydrogen, into a cream-coloured fatty substance, which on addition of fuming nitric acid yields a dirty brown and a crimson compound.

31. A solution of aniline and *quinone* in a large quantity of boiling alcohol deposits crystals of diphenyl-quinoyl-diamide, while hydroquinone remains in solution:

$$\underset{\text{Aniline.}}{2C^6H^7N} \quad + \quad \underset{\text{Quinone.}}{3C^6H^4O^2} \quad = \quad \underset{\text{Diphenyl-quinoyl-diamide.}}{\left.\begin{matrix}(C^6H^5)^2\\ (C^6H^2O^2)''\\ H^2\end{matrix}\right\}N^2} \quad + \quad \underset{\text{Hydroquinone.}}{2C^6H^6O^2.}$$

32. With *perchloroquinone* (chloranil), aniline forms diphenyl-dichloroquinoyl-diamide and hydrochlorate of aniline:

$$4C^6H^7N \quad + \quad C^6Cl^4O^2 \quad = \quad \left.\begin{matrix}(C^6H^5)^2\\ (C^6Cl^2O^2)''\\ H^2\end{matrix}\right\}N^2 \quad + \quad 2(C^6H^7N.HCl).$$

(Hofmann, Proc. Roy. Soc. xiii. 4). This latter reaction was first studied by Hesse (Ann. Ch. Pharm. cxiv. 292), who regarded the amide produced in it as dichloroquinoyl-pentaphenylpentamide, $(C^6H^5)^5(C^6\overset{\prime\prime}{C}l^2O^2)^2H^6N^5$.

**Salts of Aniline.** These salts may be regarded either as compounds of aniline with acids, or of phenyl-ammonium, $C^6H^8N$, with acid radicles: *e.g.* $C^6H^7N.HCl = C^6H^8NCl$. They are all soluble in water and alcohol, and most of them crystallise with great facility: hence the name *crystalline*, originally applied to aniline. Aniline salts are mostly colourless, but turn red when exposed to the air, especially if they are moist, acquiring at the same time a faint odour. With hypochlorite of calcium and chromic acid they exhibit the colour-reactions already described (p. 422), and when mixed with an acid, colour firwood and elder-pith deep yellow.

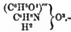
*Acetate of Aniline* is uncrystallisable.

The *bromhydrate* or *hydrobromate*, $C^6H^7N.HBr$, forms well-defined crystals usually having a violet tinge, and somewhat less soluble than the hydrochlorate. It may be sublimed without decomposition.

The *butyrate* is an oily salt, sparingly soluble in water.

*Carbonate of Aniline* does not appear to exist.

*Chlorhydrate* or *Hydrochlorate of Aniline*, $C^6H^7N.HCl$ or $C^6H^8NCl$, forms needles very soluble in water and alcohol, and capable of subliming without decomposition. It forms with *trichloride of gold* a yellow precipitate which quickly turns brown; with *platinic chloride* in cold concentrated solutions, an orange-yellow crystalline pulp; and in dilute or warm solutions, beautiful yellow needles of the chloroplatinate, $2C^6H^8NCl.Pt^{iv}Cl^4$.

*Citrate of Aniline*, $C^6H^7N.C^6H^8O^7$ or 
$\left.\begin{matrix}(C^6H^5O^4)''' \\ C^6H^8N \\ H^2\end{matrix}\right\}O^3$.—An alcoholic solution of 1 at. citric acid mixed with 1 at. aniline containing a small quantity of water, dries up, in vacuo over oil of vitriol, to a viscid brown-red mass, in which crystals begin to appear after a while, ultimately filling the entire mass. This crystalline product is triturated with a small quantity of alcohol, the liquid squeezed out through linen, the residue dissolved in strong alcohol, and the solution left over oil of vitriol till it crystallises. It forms slender needles united in rounded groups, melting at a temperature a little below 100°, very soluble in alcohol, and still more in water. Heated to a temperature between 140° and 150°, it gives off water and yields citranilic acid (i. 100).

The dibasic and tribasic citrates of aniline do not appear to crystallise. (**Pebal**, Ann. Ch. Pharm. lxxxii. 91.)

*Fluosilicate of Aniline* appears to be produced by the direct combination of aniline with fluoride of silicon, 93 pts. of aniline absorbing 63·3 pts. of the gas, and forming a slightly yellow mass which may be sublimed, dissolves sparingly in boiling alcohol, and is deposited therefrom in small shining laminæ. Water decomposes it, separating gelatinous silica. When moistened with ammonia, heated, and calcined, it leaves but a very slight residue of silica. **Laurent** and **Delbos** (Ann. Ch. Phys. [3] xxii. 101), who prepared this compound, regarded it as phenyl-fluosilicamide or fluosilicanilide.

*Iodhydrate* or *Hydriodate of Aniline*, $C^6H^8NI$, forms needles very soluble in water and alcohol, less soluble in ether.

*Mellitate of Aniline.* Aqueous aniline forms with aqueous mellitic acid a turbid liquid which gradually deposits scales resembling benzoic acid. These crystals dissolve easily in water, also in hot alcohol, but the salt no longer crystallises therefrom. It turns yellow at 105° and gives off aniline. It appears to be an acid salt, $C^4H(C^6H^8N)O^4$.

*Nitrate of Aniline*, $C^6H^7N.NHO^3$, separates after some time from a mixture of aniline and dilute nitric acid, in concentric needles, which may be purified by pressure between folds of bibulous paper. The mother-liquor is red, and an efflorescence having a fine blue colour forms on the sides of the basin. The crystals do not suffer any loss of weight at 150°; at a somewhat higher temperature, the salt sublimes unaltered, but at 190° water is given off, together with a tarry liquid from which nitraniline may be extracted by hydrochloric acid (**Béchamp**, Compt. rend. lii. 660):

$$C^6H^7N.NHO^3 \quad = \quad H^2O \quad + \quad C^6H^6(NO^2)N.$$

The salt heated with aniline is converted into nitrate of rosaniline (see APPENDIX TO PHENYLAMINES. With aqueous *chloride of iodine* containing a slight excess of iodine, it yields a bluish-green precipitate, quickly turning black, and containing (*a*) a substance soluble in sulphide of carbon, and crystallising therefrom in nearly colourless needles containing 15·7 per cent. carbon, 1·07 hydrogen, 66·23 iodine, 3·22 nitrogen, and 13·82 oxygen; (*b*) a purplish substance crystallising in laminæ, insoluble in sulphide of carbon; and (*c*) a dark-coloured amorphous body. The same products are obtained by the action of chloride of iodine on the oxalate, and probably also on other salts of aniline. (**Stenhouse**, Chem. Soc. J. xvii. 328.)

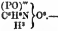
*Oxalate of Aniline*, $2C^6H^7N.C^2H^2O^4 = C^2(C^6H^8N)^2O^4$.—A boiling alcoholic solution of oxalic acid saturated with aniline, yields a magma of crystals which may be purified by washing with alcohol, and pressure between paper. From a hot saturated aqueous solution, the salt crystallises in stellate groups of oblique rhomboïdal prisms. It is anhydrous, moderately soluble in hot water, sparingly soluble in alcohol, insoluble in ether. The aqueous solution becomes acid spontaneously and deposits a brown powder on exposure to the air. When heated rather strongly, it gives off aniline, water, carbonic oxide and carbonic anhydride, and leaves a residue containing diphenyloxamide and phenyl-formamide (p. 285).

According to **Piria** (Cimento, ii. 305) perfectly pure oxalate of aniline may be heated in the oil-bath between 160° and 180° without fusion and without production of phenyl-formamide, the residue, which is perfectly white and crystalline, consisting wholly of diphenyloxamide; but oxalate of aniline in a less pure state yields phenyl-formamide as well as diphenyloxamide.

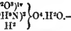
*Phenyloxamate* or *Oxanilate of Aniline* (acid), $C^8H^6(C^6H^8N)NO^3.C^8H^7NO^3$.—This salt is obtained by frequent recrystallisation of the brown crystals which are deposited from the solution of the crude product of the action of oxalic acid upon aniline in boiling water. It retains a brown tinge even after repeated crystallisation, and forms confused, often interlaced needles, destitute of lustre, sparingly soluble in cold water, easily in boiling water. When heated it gives off aniline and the products of decomposition of phenyloxamic acid. The solution mixed with hydrochloric acid does not deposit phenyloxamic acid.

*Phenylsulphamate* or *Sulphanilate of Aniline*, separates from a solution of phenylsulphamic acid in water containing aniline, the liquid first however depositing unaltered phenylsulphamic acid.

*Phosphates of Aniline.—a. Orthophosphates.—α. Dianilic*, $C^{12}H^{17}N^2PO^4 = \left.\begin{matrix}PO'''\\(C^6H^8N)^2\\H\end{matrix}\right\}O^3$.—Concentrated phosphoric acid supersaturated with aniline, solidifies immediately in a white crystalline mass, which, after being pressed, dissolved in a large quantity of boiling alcohol, strained through a hot filter, and cooled, yields flesh-coloured, nacreous, inodorous laminæ, which slightly redden litmus; they must be pressed between paper and dried on a warm tile. At 100° they turn red and give off aniline; melt at a stronger heat, and finally leave metaphosphoric acid (coloured, according to Gerhardt, by the carbonisation of a small quantity of aniline) while the aniline volatilises. They dissolve readily in water and ether, sparingly in cold alcohol, but so abundantly in hot alcohol, that the liquid solidifies on cooling. (E. C. Nicholson, Ann. Ch. Pharm. lix. 213.)



*β. Mono-anilic*, $C^6H^{10}NPO^4 = \left.\begin{matrix}(PO)'''\\C^6H^8N\\H^2\end{matrix}\right\}O^3$.—The aqueous solution of the salt α mixed with phosphoric acid till it no longer precipitates chloride of barium, yields, in a few hours, after evaporation over the water-bath, white silky needles, which must be cooled with ether and dried on a warm tile; they turn red in the air, and dissolve readily in water, alcohol and ether; in water, however, the salt α is formed at the same time. (Nicholson.)



*b. Pyrophosphate*, $C^{12}H^{18}N^2P^2O^7.H^2O = \left.\begin{matrix}(P^2O^3)^{iv}\\(C^6H^8N)^2\\H^2\end{matrix}\right\}O^4.H^2O$.—Concentrated pyrophosphoric acid obtained by decomposing pyrophosphate of lead with sulphuretted hydrogen forms with excess of aniline, a gelatinous hardening precipitate which is a mixture of tetranilic and dianilic salt. The former cannot be prepared in the pure state, but the dianilic salt is obtained by heating the mixture till solution takes place, supersaturating with acid, and evaporating over the water-bath, as a mass of needle-shaped crystals which must be pressed between paper, washed with ether, and dried in vacuo. The silky needles resemble sulphate of quinine, are strongly acid, turn red on exposure to the air, both in the solid state and in solution, and are soluble in water, but quite insoluble in alcohol and ether. (Nicholson.)

*Metaphosphate*, $C^6H^8NPO^3 = \left.\begin{matrix}PO^2\\C^6H^8N\end{matrix}\right\}O$.—The concentrated solution of glacial phosphoric acid added in large excess to aniline or to its solution in alcohol or ether, throws down a white jelly, which must be washed on the filter with ether till the odour of aniline disappears, and dried in vacuo over oil of vitriol. It is a white amorphous mass, which reddens litmus, becomes glutinous and rose-coloured on exposure to the air, and dissolves in water, but is quite insoluble in alcohol and ether. The aqueous solution is altered, by boiling in consequence of the formation of orthophosphoric acid; it dissolves metaphosphate of silver, but afterwards turns red on boiling, the silver-salt being partly reduced. (Nicholson.)

*Picrate of Aniline.*—The lemon-yellow precipitate which an excess of of alcoholic picric acid forms with aniline, dissolves in boiling alcohol and crystallises on cooling.

*Pyrotartrate of Aniline* is a crystallisable salt, the solution of which dries up to a brown syrup.

*Succinate of Aniline* forms thin oblique rectangular prisms of a pale rose colour.

*Sulphate of Aniline*, $(C^6H^8N)^2SO^4$.—A mixture of aniline and sulphuric acid immediately solidifies to a crystalline pulp which must be pressed and purified by recrystallisation. The salt is easily soluble in water, less soluble in dilute alcohol, still less in absolute alcohol, insoluble in ether. An alcoholic solution saturated at the boiling heat solidifies on cooling. It may be heated to 100° without alteration. When carefully raised to a higher temperature, it gives off water and aniline, and is converted into phenylsluphamic acid. At a still higher temperature, it suffers further decomposition, gives off sulphurous anhydride and sulphite of aniline, and leaves charcoal.

*Sulphite of Aniline* is obtained as a radiate crystalline mass, by treating aniline with sulphurous anhydride ( ? moist).

*Sulphobenzolate* or *Sulphophenylate of Aniline*, $C^6H^5(C^6H^8N)SO^3$, obtained by dropping aniline into a hot solution of sulphobenzolic acid (*q. v.*), crystallises in long silky needles arranged in stellate groups, and generally exhibiting a reddish tint.

They melt at 201°, and the fused salt solidifies in a stellate crystalline mass; it sublimes below the melting point in colourless crystals. Dissolves readily in water and alcohol, sparingly in ether. (Gericke, Ann. Ch. Pharm. c. 217.)

*Sulphocyanate of Aniline*, $C^6H^7N.CNHS$.—Aqueous sulphocyanic acid saturated with aniline deposits on evaporation, red oily drops which gradually solidify in the crystalline form. The crystalline mass melts when gently heated; then gives off sulphuretted hydrogen and sulphide of ammonium, with violent ebullition; and when more strongly heated, yields an oily distillate of sulphide of carbon and sulphide of ammonium together with diphenylsulphocarbamide, and leaves a pale resinous residue:

$$2(C^6H^7N.CNHS) \quad = \quad \underset{\substack{\text{Diphenylsulpho-}\\ \text{carbamide.}}}{C^{13}H^{12}N^2S} \quad + \quad \underset{\substack{\text{Sulphocyanate}\\ \text{of ammonium.}}}{CN^2H^4S.}$$

But the latter is further resolved at the given temperature into sulphide of carbon, sulphide of ammonium, and a residue of mellone, to which however an aniline-compound adheres. (Laurent and Gerhardt.)

*Tartrate of Aniline.*—Aqueous tartaric acid solidifies in contact with aniline. The salt crystallises from hot water in needles. (Hofmann.)

*Compounds of Aniline with Metallic Salts.*—Aniline unites directly with a considerable number of metallic salts forming compounds which may be regarded as chlorides, sulphates, &c., of phenylammoniums containing metals. Gerhardt, by treating aniline with mercuric chloride, obtained the salt $2C^6H^7N.Hg''Cl^2$ or $C^{12}H^{12}Hg''N^2.Cl^2$, and a similar compound with chloride of palladium. More recently this class of compounds has been examined by H. Schiff (Ann. Ch. Pharm. cxxv. 360; cxxvii. 337.—Bull. Soc. Chim. v. 65), who has prepared a considerable number of them. They may be represented by the general formula:

$$nC^6H^7N.M^{(n)}X^n \quad = \quad \left.\begin{matrix} M^{(n)} \\ (C^6H^5)^n \\ H^n \end{matrix}\right\} N^n.X^n\,;$$

in which $M^{(n)}$ denotes an *n*-atomic metal, and X a monatomic salt-radicle, such as Cl, $NO^3$, &c., $X^2$ being of course replaceable by $X''$, $X^3$ by $X'''$, &c. *e. g.*:

Sulphate of Zincodiphenyl-diammonium, $2C^6H^7N.Zn''Cl^2 = (C^6H^5)^2H^2Zn''N^2.Cl^2$.
Chloride of Stibio-triphenyl-triammonium, $3C^6H^7N.Sb'''Cl^3 = (C^6H^5)^3H^3Sb'''N^3.Cl^3$.
Chloride of Stannico-tetraphenyl-tetrammonium, $4C^6H^7N.Sn^{iv}Cl^4 = (C^6H^5)^4H^4Sn^{iv}N^4.Cl^4$.

These salts are colourless, permanent in the air, and crystallise well. Some of them are soluble in water; some may be fused, sublimed, or distilled without decomposition.

For the description of the individual compounds, see PHENYLAMMONIUMS.

### SUBSTITUTION-DERIVATIVES OF ANILINE.

The derivatives of monophenylamine or aniline, $\left.\begin{matrix} C^6H^5 \\ H^2 \end{matrix}\right\} N$, may be arranged in two well-defined groups, namely, 1. Those which are formed by substitution of bromine, chlorine, cyanogen, iodine, nitrogen or nitryl for one or more atoms of hydrogen belonging to the phenyl-radicle $C^6H^5$; *e.g. bromaniline*, $\left.\begin{matrix} C^6H^4Br \\ H^2 \end{matrix}\right\} N$, *dinitraniline*, $\left.\begin{matrix} C^6H^3(NO^2)^2 \\ H^2 \end{matrix}\right\} N$.

2. Those which are formed by substitution of alcohol-radicles or acid-radicles for the extra-radical or typic hydrogen, *e.g. ethylaniline*, $\left.\begin{matrix} C^6H^5 \\ C^2H^5 \\ H \end{matrix}\right\} N$, *phenylacetamide*, $\left.\begin{matrix} C^6H^5 \\ C^2H^3O \\ H \end{matrix}\right\} N$, &c.

### I. DERIVATIVES OF ANILINE FORMED BY REPLACEMENT OF HYDROGEN WITHIN THE PHENYL-RADICLE.

The radical hydrogen of aniline may be replaced, to the extent of 1, 2, or 3 atoms by chlorine, bromine, or nitryl. The trichloro- and tribromo-compounds are formed by the direct action of chlorine or bromine on aniline; those containing only 1 or 2 at. chlorine or bromine, as well as the nitro-compounds, are not obtained directly from aniline. These substitution-compounds are less basic in proportion to the number of hydrogen-atoms replaced. Mono- and di-bromo-phenylamine are basic; so likewise are the monochlorinated and mononitro-compounds; but the tribromo-, dichloro-, trichloro-, dinitro- and trinitro-phenylamines are neutral. One atom of radical hydrogen in aniline may also be replaced by iodine, and by cyanogen. Iodophenylamine, $C^6H^6IN$, is obtained by the direct action of iodine on aniline; and cyanophenylamine or cyanilide, $C^7H^6N^2 = C^6H^6(CN)N$, by that of chloride of cyanogen on an ethereal solution of aniline cooled by ice. Iodophenylamine is basic; cyanophenylamine is neutral.

In connection with the last-mentioned compound must also be mentioned a base called cyananiline, produced by the direct action of cyanogen on aniline, and containing $C^7H^7N^2 = C^6H^7N.Cy$, that is to say, the elements of cyanogen and aniline united without elimination of hydrogen.

There is also a group of compounds called azophenylamines in which 1 at. nitrogen takes the place of 3 at. hydrogen.

The monochloro-, bromo-, and nitro-phenylamines are susceptible of two isomeric modifications.

### *Azophenylamines.*

These are bases produced by the action of nitrous acid on aniline, and on the bromo-, chloro-, iodo-, and nitro-phenylamines above mentioned, and derivable therefrom by the substitution of 1 at. nitrogen for 3 at. hydrogen. They may also be regarded as formed from benzene, $C^6H^6$, and its derivatives, bromobenzene, nitrobenzene, &c., by the substitution of 1 at. nitrogen for 1 at. hydrogen; and this is the view of their constitution entertained by Griess, by whom they have all been discovered and investigated (Phil. Trans. 1864, Pt. iii. p. 667).

**Azophenylamine**[*] or **Azaniline**, $C^6H^4N^2 = \left.\begin{matrix}C^6H^4N'''\\H^2\end{matrix}\right\}N$, or *Diazobenzene*, $\left.\begin{matrix}C^6H^4N'\\H\end{matrix}\right\}$.—This base is obtained as a nitrate: 1. By the action of nitrous acid on nitrate of aniline:

$$C^6H^7N \quad + \quad NHO^2 \quad = \quad C^6H^4N^2 \quad + \quad 2H^2O.$$

Nitrate of aniline ground to a paste with water is submitted to the action of nitrous acid gas in a vessel externally cooled so as to prevent the temperature rising above 30°. The salt then gradually dissolves, and as soon as it has all disappeared, the solution is filtered to remove traces of a brown resin, then mixed with 3 vol. strong alcohol, and ether is added to precipitate the nitrate of azophenylamine. The precipitated crystals are separated from the mother-liquor by filtration, and decolorised by solution in cold dilute alcohol, and reprecipitation with ether.

2. By the action of nitrous acid on azodiphenyldiamine, $\left.\begin{matrix}(C^{12}H^7N''')''\\H^4\end{matrix}\right\}N^2$, dissolved in ether and mixed with nitric acid:

$$\underset{\substack{\text{Azodiphenyl-}\\\text{diamine.}}}{C^{12}H^{11}N^3} \quad + \quad NHO^2 \quad + \quad 2NHO^3 \quad = \quad \underset{\substack{\text{Nitrate of azophenyl-}\\\text{amine.}}}{2(C^6H^4N^2.NHO^3)} \quad + \quad 2H^2O.$$

3. By the direct action of nitrous acid on aniline mixed with 4 vol. alcohol, in which case it is probable that azodiphenyldiamine is first formed (p. 460) and then converted into nitrate of azophenylamine as above.

4. By the action of nitrous acid on nitrate of ethylaniline:

$$C^6H^6(C^2H^5)N.NHO^3 \quad + \quad NHO^2 \quad = \quad C^6H^4N^2.NHO^3 \quad + \quad C^2H^6O \quad + \quad H^2O.$$

A very concentrated solution of nitrate of azophenylamine mixed with very strong caustic potash and evaporated over the water-bath, yields a compound of azophenylamine with potash, $C^6H^4N^2.KHO$; and the aqueous solution of this compound mixed with acetic acid, deposits azophenylamine as a thick yellow oil, having a peculiar odour, and remarkable for its extreme instability. It soon begins to give off nitrogen, and is rapidly converted into a brownish-red substance; the decomposition is attended with considerable rise of temperature, which, when large quantities are concerned, may give rise to dangerous explosions. Ether dissolves it instantly, with violent evolution of gas, and forms a red solution.

COMPOUNDS OF AZOPHENYLAMINE.—Azophenylamine unites both with acids, and with other bases organic and inorganic; but the compounds are best obtained by indirect methods.

*Bromine-compounds.*—The *hydrobromate*, $C^6H^4N^2.HBr$, is produced, together with tribromaniline, by the action of bromine on azodiphenyldiamine, as shown by the equation:

$$C^{12}H^{11}N^3 \; + \; Br^6 \; = \; C^6H^4N^2.HBr \; + \; C^6H^4Br^3N \; + \; 2HBr.$$

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[*] The term azophenylamine was applied by Gerhardt to Zinin's semibenzidam, $C^6H^8N^2$; but this body has the composition of amidophenylamine, $C^6H^6(NH^2)N$, or of phenylene-diamine, $\left.\begin{matrix}(C^6H^4)''\\H^4\end{matrix}\right\}N^2$, (*q. v.*).

On adding an ethereal solution of bromine by drops to a moderately strong solution of azodiphenyldiamine, a crystalline precipitate of hydrobromate of azophenylamine is produced, while tribromaniline remains in solution. The crystals must be quickly washed with ether and dried over oil of vitriol.

Hydrobromate of azophenylamine crystallises in white nacreous scales easily soluble in *water*, less soluble in *alcohol*, insoluble in *ether*. The solutions have a strong acid reaction. The salt is very unstable, decomposing spontaneously with a peculiar odour, and exploding with violence by heat, friction or pressure. The aqueous solution treated with moist *chloride of silver* yields bromide of silver and hydrochlorate of azophenylamine or chloride of azophenylammonium.

*Bromoplatinate*, $2(C^6H^4N^2.HBr)Pt^{iv}Br^4$.—Obtained as an insoluble reddish-yellow precipitate on mixing platinic bromide with aqueous nitrate of azophenylamine. It is decomposed by heating with carbonate of sodium, in the same manner as the chloroplatinate (*infra*) yielding bromobenzene.

*Perbromide of Azophenylammonium*, $C^6H^5N^2Br^3 = \left.\begin{matrix}(C^6H^5N''')' \\ H^3\end{matrix}\right\}NBr^3$.—This compound, probably analogous in constitution to the tri-iodide of tetrethylammonium, is produced by the action of bromine on nitrate of azophenylamine. On adding a small quantity of bromine-water to an aqueous solution of the nitrate, a white crystalline precipitate of tribromophenic acid is usually obtained, owing to the presence of a small quantity of phenol formed from the decomposition of the nitrate by water. On removing this precipitate as quickly as possible and adding a large excess of bromine-water to the filtrate, perbromide of azophenylammonium separates as a brownish-red oil, which when separated from the mother-liquor quickly solidifies in a crystalline mass; it may be purified by washing with ether, or by dissolving it in cold alcohol, leaving the solution to evaporate spontaneously in shallow vessels, and then washing the residue with a little ether to remove an oily product of decomposition.

Perbromide of azophenylammonium crystallises in yellow plates insoluble in *water*, rather difficultly soluble in *alcohol*, insoluble in *ether*. It is comparatively stable in the dry state, but decomposes quickly in alcoholic solution. When heated it gives off bromine and nitrogen and is converted into bromobenzene:

$$C^6H^5N^2Br^3 \;=\; C^6H^5Br + N^2 + Br^2.$$

In decomposing large quantities of the perbromide in this manner, it should be mixed with carbonate of sodium, otherwise a violent explosion is likely to occur. Bromobenzene is likewise formed on heating the perbromide with alcohol, and separates as a heavy oil on adding water to the solution.

With aqueous *ammonia* the perbromide yields **azophenylene-diamine** (diazobenzolimide of Griess) and bromide of ammonium:

$$\underset{\text{Perbromide.}}{C^6H^5N^2Br^3 + 4NH^3} \;=\; \underset{\text{Azophenylene-diamine.}}{\left.\begin{matrix}(C^6HN''')'' \\ H^4\end{matrix}\right\}N^2} + 3NH^4Br.$$

***Chlorine-compounds***.—The *hydrochlorate* is obtained by treating an aqueous solution of the nitrate with moist chloride of silver.

*Chloroaurate*, $C^6H^4N^2.HCl.AuCl^3$.—Obtained on adding trichloride of gold to an aqueous solution of the nitrate, as a light yellow crystalline precipitate insoluble in water, but soluble in alcohol, from which it crystallises, on cooling, in small golden yellow plates: it cannot however be recrystallised without loss, and is completely decomposed by continued boiling with alcohol.

*Sulphydric acid* gas passed through water in which this gold-salt is suspended, converts it into trisulphide of gold, and a volatile oily liquid isomeric with phenylmercaptan (p. 418.):

$$C^6H^4N^2 + H^2S \;=\; C^6H^6S + N^2.$$

This liquid has an odour of mercaptan, but is not precipitated by acetate of lead or nitrate of silver. A small portion of the azophenylamine undergoes at the same time a different decomposition, resulting in the formation of aniline:

$$C^6H^4N^2 + 3H^2S \;=\; C^6H^7N + NH^3 + S^3.$$

Sulphydric acid passed over the gold-salt spread in a thin layer over the inside of a glass tube, decomposes it into hydrochloric acid, trisulphide of gold and azophenylamine; the decomposition of larger quantities is attended with explosion.

*Chloroplatinate*, $2(C^6H^4N.HCl).Pt^{iv}Cl^4$.—Precipitated on adding platinic chloride to a rather concentrated solution of the nitrate, in fine yellow prisms almost insoluble in alcohol and ether. They are moderately stable, but when kept for some time acquire a brownish colour, and are gradually but completely decomposed. The salt deflagrates when heated, but if mixed with a large excess of carbonate of sodium, barium, calcium, &c., and heated in a sand-bath, it is quickly decomposed into chlorobenzene, metallic platinum, chlorine, and nitrogen:

$$2(C^6H^4N^2.HCl)Pt^{iv}Cl^4 \;=\; 2C^6H^5Cl + Pt + Cl^4 + N^4.$$

*Nitrate of Azophenylamine*, $C^6H^4N^2.NHO^3$.—This salt, the preparation of which has been already described, crystallises in long white needles very soluble in *water*, less soluble in *alcohol*, almost insoluble in *ether*, and in *benzene*. It may be dried without alteration over oil of vitriol. When heated even below 100°, it explodes with fearful violence, far surpassing that of fulminating mercury or iodide of nitrogen. The explosion of a gramme of it causes a concussion like that produced by firing a pistol; a somewhat larger quantity exploded on an iron slab several lines thick smashed it to atoms. Friction, pressure and percussion also cause it to explode. The smallest particles of it accidentally dropped on the floor of a room, and trodden upon when dry, give rise to a series of explosions attended with flashes of light.

Nitrate of azophenylamine is resolved by boiling with *water*, into phenol, nitric acid and free nitrogen:

$$C^6H^4N^2.NHO^3 + H^2O \;=\; C^6H^6O + NHO^3 + N^2.$$

By distillation with *alcohol*, it is resolved into dinitrophenic acid, benzene, and aldehyde, together with water and free nitrogen:

$$2(C^6H^4N^2.NHO^3) + C^2H^6O \;=\; C^6H^4(NO^2)^2O + C^6H^6 + C^2H^4O + H^2O + N^4.$$

A cold aqueous solution of the nitrate left in contact with levigated *carbonate of barium*, slowly gives off nitrogen and is converted, after some days, into a mixture of two compounds of azophenylamine with phenol: viz. $C^{12}H^{10}N^2O = C^6H^4N^2.C^6H^6O$ and $C^{18}H^{14}N^4O = 2C^6H^4N^2.C^6H^6O$ (*vid. inf.*), the mode of their formation being as follows:

$$2C^6H^4N^2 + H^2O \;=\; C^{12}H^{10}N^2O + N^2$$
$$3C^6H^4N^2 + H^2O \;=\; C^{18}H^{14}N^4O + N^2.$$

On mixing very concentrated aqueous nitrate of azophenylamine and *caustic potash*, a compound of azophenylamine with potassic hydrate, $C^6H^4N^2.KHO$, is produced; but on mixing dilute aqueous solutions of the two bodies, a yellow liquid is obtained, which has a peculiar odour, soon begins to give off nitrogen, and deposits a reddish-brown substance having the composition $C^{24}H^{18}N^2O$:

$$4C^6H^4N^2 + H^2O \;=\; C^{24}H^{18}N^2O + N^6.$$

The reaction is very slow at common temperatures, but takes place quickly on heating the liquid, the reddish-brown substance being then separated as a resinous semifluid mass, quite insoluble in water, only slightly soluble in alcohol, even at the boiling heat, but easily soluble in ether, and remaining as a resin on evaporating the ether. Its powder is strongly electric. When boiled with nitric acid, it yields a yellowish crystalline body.

*Alcoholic potash* added to the aqueous nitrate of azophenylamine produces a more complicated reaction, yielding benzene and phenyl, in addition to the reddish-brown substance:

$$\underset{\text{Azophenylamine.}}{C^6H^4N^2} + \underset{\text{Alcohol.}}{C^2H^6O} \;=\; \underset{\text{Benzene.}}{C^6H^6} + \underset{\text{Aldehyde.}}{C^2H^4O} + N^2.$$

$$2C^6H^4N^2 + C^2H^6O \;=\; \underset{\text{Phenyl.}}{C^{12}H^{10}} + C^2H^4O + N^4.$$

On heating the liquid in a retort, the benzene passes over with the alcohol and may be separated by addition of water, while the phenyl, being less volatile, distils over after the alcohol and crystallises in the receiver. It melts at 70°, and resembles in every respect the phenyl obtained by Fittig (p. 409).

Dilute aqueous *ammonia* added to an aqueous solution of nitrate of azophenylamine, forms a brown mass separable by alcohol into an easily soluble and a sparingly soluble portion. The latter is identical with the compound $C^{24}H^{18}N^2O$, produced by the action of potash; the former is azodiphenyl-diamine, $C^{12}H^{11}N^3$, produced as shown by the equation:

$$2(C^6H^4N^2.NHO^3) + 3NH^3 \;=\; C^{12}H^{11}N^3 + 2(NH^4.NO^3).$$

With *bromine*, nitrate of azophenylamine yields perbromide of azophenylammonium. With *auric* and *platinic* chlorides, it forms precipitates of the chloroaurate and chloroplatinate of azophenylamine.

With *aniline* in aqueous solution it forms azodiphenyl-diamine and nitrate of aniline:

$$C^6H^4N^2.NHO^3 + 2C^6H^7N \;=\; C^{12}H^{11}N^3 + C^6H^7N.NHO^3.$$

In like manner with *bromaniline* it yields bromazodiphenyldiamine, $C^{12}H^{10}BrN^{3}$; and with *naphthylamine*, it forms azonaphthyl-phenyl-diamine (see PHENYL-DIAMINES, p. 454):

$$\left.\begin{matrix}C^6H^5N'''\\ H^2\end{matrix}\right\}N \;+\; \left.\begin{matrix}C^{10}H^7\\ H^2\end{matrix}\right\}N \;=\; \left.\begin{matrix}(C^{16}H^9N''')''\\ H^4\end{matrix}\right\}N^3.$$

*Oxybenzamate of Azophenylamine*, $C^{13}H^{11}N^3O^2 = C^6H^4N^2.C^7H^7NO^2$, or *Azophenyl-oxybenzamic acid*, $\left.\begin{matrix}(C^6H^4N''')'\\ (C^7H^4O)''\\ H^3\end{matrix}\right\}\begin{matrix}N^2\\ O.\end{matrix}$—*Diazobenzol-amidobenzoic acid* (Griess).

—Obtained by mixing an aqueous solution of 1 at. nitrate of azophenylamine with 2 at. oxybenzamic acid, separating as a yellow crystalline precipitate, the ethereal solution of which deposits yellow crystals, to be purified by washing with cold water:

$$\underset{\text{Nitrate of Azophenylamine.}}{C^6H^4N^2.NHO^3} + \underset{\text{Oxybenzamic acid.}}{2C^7H^7NO^2} = \underset{\text{Oxybenzamate of Azophenylamine.}}{C^{13}H^{11}N^3O^2} + \underset{\text{Nitrate of Oxybenzamic acid.}}{C^7H^7NO^2.NHO^3.}$$

It forms small indistinct plates or crystalline grains, nearly insoluble in *water*, very sparingly soluble in *alcohol*, easily soluble in *ether*. Heated on platinum-foil, it melts and is rapidly decomposed, with violent evolution of gas. Cold dilute *mineral acids* act upon it but slowly, but decompose it speedily with aid of heat. *Acetic acid* even when highly concentrated has no action upon it in the cold, but destroys it when heated. Solutions of *ammonia*, *potash*, and *carbonate of potassium* dissolve it readily, with yellow colour.

Azophenyl-oxybenzamic acid exhibits, with *bases*, the behaviour of a dibasic acid, uniting with them in two preparations. All its salts are comparatively stable: those which are soluble in water, the potassium-salt for example, will even bear recrystallisation. With the oxides of silver and barium it forms insoluble precipitates.

Like most amic acids it exhibits basic as well as acid characters. On mixing its ethereal solution with an alcoholic solution of platinic chloride, a *chloroplatinate*, $C^{13}H^{11}N^3O^2.2HCl.Pt^{iv}Cl^4$, is precipitated in small indistinct yellowish-white plates.

Azophenylamine forms similar compounds with *paraoxybenzamic* acid (p. 352), *oxyanisamic* acid, &c., which are obtained in like manner by acting on nitrate of azophenylamine with the respective acids.

*Phenates of Azophenylamine.*—Two of these compounds, containing respectively the elements of 1 and 2 at. azophenylamine with 1 at. phenol, are produced, as already observed (p. 432), by the action of carbonate of barium on a cold aqueous solution of nitrate of azophenylamine. Nitrogen is then slowly evolved, and a reddish-brown mass is formed, consisting of the two compounds just mentioned together with the excess of carbonate of barium; and on filtering off the solution containing nitrate of barium, removing the excess of carbonate by hydrochloric acid, and treating the residue with cold alcohol, the compound containing the larger proportion of phenol dissolves out, while the more basic compound remains for the most part undissolved.

*Monoazophenylamic Phenate*, $C^{12}H^{10}N^2O = C^6H^4N^2.C^6H^6O$, or *Azodiphenylamic acid*, $\left.\begin{matrix}(C^{12}H^7N''')''\\ H^3\end{matrix}\right\}\begin{matrix}N\\ O.\end{matrix}$—To purify this compound, the alcoholic solution obtained as above is evaporated, the residue is treated with ammonia, and the deep yellow solution after being filtered, is decomposed with hydrochloric acid. Azodiphenylamic acid is then precipitated in crystals which may be further purified by repeated crystallisation from weak spirit. It is almost insoluble in cold *water*, slightly soluble in boiling water, from which it crystallises on cooling in small but well-formed rhombic prisms of a fine yellow colour with a tinge of violet. From *alcohol* and *ether* (in which it dissolves very easily) it usually crystallises in brittle brownish-yellow nodules. It melts at 148° to a brownish-yellow oil which cannot be volatilised without decomposition, but is destroyed at a higher temperature, with formation of yellow vapour.

This compound possesses slight acid properties, and forms saline compounds with certain metals, but it is not capable of decomposing carbonates. On evaporating its solution with aqueous ammonia, the whole of the ammonia is driven off. It forms a scarlet precipitate with nitrate of silver.

*Diphenylamic Phenate*, $C^{18}H^{14}N^4O = 2C^6H^4N^2.C^6H^6O$, or *Azotriphenylamic acid*, $\left.\begin{matrix}(C^{18}H^9N''')'''\\ H^5\end{matrix}\right\}\begin{matrix}N^3\\ O.\end{matrix}$—This compound may be obtained pure by recrystallising the less soluble portion of the reddish brown substance above mentioned, once or twice from strong alcohol, then dissolving it in ether, and leaving the solution to evaporate. Sometimes however it is contaminated with traces of another substance, to remove which it must be dissolved in caustic potash, and the filtered alkaline solution precipitated by hydrochloric acid. It crystallises in brownish-red needles or plates, easily soluble in *ether*, sparingly in cold *alcohol* and in hot *water*. It melts at 113° and

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decomposes at a higher temperature like the preceding compound. It is nearly neutral but dissolves easily in *potash*, forming a ruby-red solution, with difficulty in aqueous *ammonia*, and not at all in aqueous carbonate of potassium. It is likewise insoluble in dilute acids, but dissolves in concentrated acids, forming blood-red solutions which decompose when heated.

*Sulphate of Azophenylamine*, $C^6H^4N^2.SH^2O^4$. This salt may be obtained by the action of nitrous acid on sulphate of aniline suspended in water, or more conveniently by treating a concentrated aqueous solution of the nitrate with dilute sulphuric acid, mixing the resulting solution with 3 vol. absolute alcohol, and then with ether, which causes the sulphate of azophenylamine, together with some water, to separate in a layer at the bottom, while the liberated nitric acid, together with excess of sulphuric acid, remains mixed with the supernatant alcohol and ether. This latter is decanted, the solution of the sulphate once more treated with absolute alcohol and precipitated by ether, and the precipitated liquid placed in flat dishes over oil of vitriol. It then solidifies to a magma of crystals, which must be washed on a filter with a mixture of alcohol and ether, to remove any traces of sulphuric acid and phenol produced by partial decomposition of the sulphate, then dissolved in cold weak alcohol, precipitated by ether, and the crystals quickly dried over oil of vitriol.

Sulphate of azophenylamine crystallises in prisms, which dissolve readily in water, with difficulty in absolute alcohol, and not at all in ether. The aqueous and alcoholic solutions decompose, with evolution of gas, on boiling. When exposed to the air, the salt rapidly absorbs moisture, becomes liquid, and gradually decomposes. When heated alone, it deflagrates feebly at about 100°.

Sulphate of azophenylamine heated with concentrated *sulphuric acid*, gives off the whole of its nitrogen and is converted into disulphophenylenic acid, $C^6H^6S^2O^6 = C^6H^4.2SH^2O^4$ (see SULPHURIC ETHERS):

$$C^6H^4N^2.SH^2O^4 \quad + \quad SH^2O^4 \quad = \quad C^6H^6S^2O^6 \quad + \quad N^2.$$

COMPOUNDS OF AZOPHENYLAMINE WITH BASES.—*α*. With *Hydrate of Potassium*, $C^6H^4N^2.KHO$. On adding a very concentrated solution of nitrate of azophenylamine, drop by drop, to strong aqueous potash, a yellowish liquid is obtained, having a peculiar aromatic odour and solidifying by evaporation over the water-bath to a crystalline mass, which is a mixture of the compound of potassic hydrate and azophenylamine with nitrate of potassium, and a brownish-red body, the result of a secondary reaction. The crystalline mass is put into a strong linen cloth and well squeezed between porous stones, to remove the excess of potash; the dry cake is then treated with absolute alcohol, which readily dissolves the compound of potassic hydrate and azophenylamine, leaving the nitre undissolved; the alcoholic filtrate which has an intense reddish-brown colour (due to the above-mentioned secondary product) is evaporated over the water-bath; and the residue is once more pressed and washed with a mixture of alcohol and ether to remove the reddish-brown substance. By again pressing the nearly white cake thus obtained, dissolving it in a small quantity of absolute alcohol, filtering, and adding a sufficient amount of ether, the compound is precipitated in small white crystals which must be immediately dried over oil of vitriol.

It crystallises in small white soft plates, becomes reddish by exposure to the air, is easily soluble in *water* and in *alcohol*, insoluble in ether. The solutions have a strong alkaline reaction. The freshly prepared aqueous solution is but slightly coloured; but by keeping for a short time it acquires a yellow colour, and ultimately deposits a reddish-yellow substance. The decomposition does not appear to be much accelerated by boiling. The dry substance is very stable. When heated alone it explodes with a slight report at a little above 130°.

*β*. With *Hydrate of Silver*, $C^6H^4N^2.AgHO$. Obtained as a white or slightly chocolate-coloured precipitate by heating a freshly-prepared solution of the potassium compound with nitrate of silver. After removing the mother-liquor, the precipitate is thoroughly washed with water, dried by pressing between filter-paper, and finally over oil of vitriol. It is insoluble in all the ordinary neutral solvents. Nitric acid, even when cold, dissolves it with great facility. It is remarkably stable, not exhibiting the slightest sign of decomposition even after being kept for weeks. It explodes with some violence when heated.

*γ*. With *Hydrate of Barium*. Precipitated by adding the solution of a very soluble barium-salt to a moderately concentrated solution of the potassium-compound, in white, microscopic, indistinct needles or plates, which become yellowish from gradual decomposition. It is sparingly soluble in water.

*δ*. The compound of azophenylamine with *hydrate of zinc* is a white amorphous powder, insoluble in water. The *lead-compound* is also a white powder, but quickly turns yellow. With *cupric sulphate* a brown precipitate changing to green is obtained. Mercuric chloride gives no precipitate.

COMPOUNDS OF AZOPHENYLAMINE WITH OTHER ORGANIC BASES.—Azophenylamine, as already observed (p. 432), unites with aniline, bromaniline, and naphthylamine, forming compounds which have the constitution of phenyldiamines, and will be described under that head (p. 459).

## 2. *Bromophenylamines.*

**Monobromophenylamine** or **Bromaniline,** $C^6H^6BrN = \left.\begin{matrix}C^6H^4Br\\H^2\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. liii. 42.—E. J. Mills, Proc. Roy. Soc. x. 589.—Griess, Phil. Trans. 1864 [3], 713).—Of this base there are two isomeric modifications, α and β, exactly resembling one another in their chemical deportment, but distinguished by certain physical properties, both in the free state and in combination with acids.

Alpha-bromaniline is prepared: 1. By heating bromisatin with potash, just as aniline itself is obtained from isatin (p. 420):

$$C^6H^4BrNO^2 \quad + \quad 4KHO \quad = \quad C^6H^6BrN \quad + \; . \; 2K^2CO^3 \quad + \quad H^2.$$

The distillation is continued till the residue is nearly dry, and gives off a brown oil which no longer solidifies. The oily drops which passed over at the beginning of the distillation and have solidified in the crystalline form, are then washed on a filter with water and recrystallised from boiling alcohol (Hofmann).—2. By distilling dibromophenylacetamide (p. 418) with potash (Mills).—3. By the action of nascent hydrogen (generated by the action of zinc and sulphuric acid) on an alcoholic solution of azobromophenylene-diamine:

$$\left.\begin{matrix}(C^6BrN''')''\\H^4\end{matrix}\right\}N^2 \quad + \quad H^6 \quad = \quad \left.\begin{matrix}C^6H^4Br\\H^2\end{matrix}\right\}N \quad + \quad 2NH^3.$$

When the addition of water no longer forms a precipitate, the bromaniline may be separated by evaporating the alcoholic solution over a water-bath, and distilling with potash (Griess).—4. By the action of sulphide of ammonium on β-bromonitrobenzene (p. 416).

β-Bromaniline is obtained by the action of sulphide of ammonium on α-bromonitrobenzene (p. 416).

*Properties.*—Alpha-bromaniline crystallises in colourless, regular octahedrons, exactly like chloraniline (Hofmann); that prepared from phenylacetamide sometimes crystallises in needles (Mills); always in octahedrons (Griess). It melts at 50° (Hofmann); 57° (Griess); and solidifies again at 46° (Hofmann). In odour and taste it resembles chloraniline..

β-bromaniline is an oil which does not solidify even in winter. (Griess.)

Bromaniline (both varieties) is easily reduced to aniline by *potassium-amalgam.* With excess of *bromide of ethyl,* it is quickly converted into hydrobromate of ethylbromaniline, $C^8H^{10}BrN.HCl$. Its aqueous solution imparts a violet colour to aqueous *chloride of lime,* weaker than that produced by aniline, but stronger than that produced by chloraniline. Its salts colour chloride of lime red-brown and firwood yellow. Bromaniline dissolves readily in *sulphide of carbon.*

*Hydrochlorate of α-bromaniline,* $C^6H^6BrN.HCl$, crystallises from boiling water in nacreous radiated fibres, but by evaporation over oil of vitriol, in well-defined monoclinic prisms (Hofmann). Hydrochlorate of β-bromaniline forms white nacreous brilliant plates, which are readily soluble in water and alcohol, and quickly turn red when exposed to the air. (Griess.)

*The chloroplatinate of α-bromaniline,* $2C^6H^6BrN.H^2Cl^2.Pt^{iv}Cl^4$, precipitated on mixing hydrochlorate of α-bromaniline with platinic chloride, closely resembles the corresponding compound of chloraniline (Hofmann). The corresponding salt of *β-bromaniline* crystallises in yellow, often well-formed prisms, much more soluble than the slender highly-lustrous plates of the α-salt. (Griess.)

*The oxalate,* $2C^6H^6BrN.C^2H^2O^4$, precipitated from alcoholic α-bromaniline by aqueous oxalic acid, and crystallised from boiling water, forms indistinct crystals, sparingly soluble in water and alcohol.

**Dibromophenylamine** or **Dibromaniline,** $C^6H^5Br^2N = \left.\begin{matrix}C^6H^3Br^2\\H^2\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. liii. 47.—Griess, *ibid.* cxxi. 257.)—Prepared: 1. By distilling dibromisatin with caustic potash, washing the distilled and crystallised oil with water, and crystallising from boiling alcohol (Hofmann).—2. By adding bromine to phenylacetamide suspended in water, till it is converted into a reddish resinous mass, consisting mainly of dibromophenylacetamide $(C^6H^3Br^2)(C^2H^3O)HN$, and subjecting this product to distillation with potash. Dibromaniline then passes over in oily drops which solidify to white needles. On dissolving this product in warm moderately-strong hydrochloric acid, any tribromaniline that may be present remains undissolved, and on evaporating the hydrochloric acid solution to dryness, and treating the residue with hot water, dibromaniline alone remains undissolved, while traces of hydrochlorate of monobromaniline are taken up by the water. (Griess.)

Large, flat, somewhat rhombic prisms, melting between 50° and 60° to a dark-coloured oil, which often remains liquid long after cooling, but then crystallises suddenly on agitation (Hofmann). Crystallises from alcohol in needles or long laminæ, which melt at 79·5°. (Griess.)

Dibromaniline dissolves sparingly in *water*, forming a liquid which becomes turbid on cooling and gradually deposits slender needles; it is soluble in *alcohol*. It is a very weak base; its solution in *acids* colours firwood yellow; it is precipitated by alkalis. It forms crystallisable salts, which however are less stable than those of bromaniline.

The solution of dibromaniline in boiling *hydrochloric acid*, yields on cooling, laminæ containing 13·31 per cent. hydrochloric acid; when they are dissolved in water, part of the base separates in thin oily drops; and the solution evaporated under a bell-jar over lime, which abstracts the greater part of the hydrochloric acid, deposits nearly pure crystalline dibromaniline (Hofmann). The hydrochloric acid solution forms a crystalline orange-yellow precipitate with platinic chloride. The *hydrochlorate*, $C^6H^5Br^2N$, crystallises in tufts resembling palm-branches; the easily decomposible *platinum-salt*, $2C^6H^5Br^2N.H^2Cl^2.Pt^{iv}Cl^4$, in yellow prisms. (Griess.)

**Tribromophenylamine** or **Tribromaniline.** $C^6H^4Br^3N = \left.\begin{matrix}C^6H^2Br^3\\H^2\end{matrix}\right\}N.$ (Fritzsche, J. pr. Chem. xxviii. 204.—Hofmann, Ann. Ch. Pharm. liii. 50).—*Bromaniloïd* (Fritzsche).—*Preparation.* 1. Dry bromine is mixed with aniline in such proportion that the mixture solidifies completely after a while in the crystalline form, after which alcohol is added, and also more bromine till its odour becomes permanent. The greenish-grey crystalline magma of tolerably pure tribromaniline is then separated by filtration from the greenish-yellow alcoholic liquid, which contains hydrobromic acid and the decomposition-products of the alcohol, and deposits more tribromaniline when mixed with water; after which it is washed on the filter with alcohol and dissolved in hot alcohol: the solution thus obtained yields nearly colourless crystals (Fritzsche).—2. The aqueous solution of an aniline-salt is mixed with aqueous bromine, which disappears and produces a white turbidity and precipitation of microscopic needles, the addition of bromine being continued till the precipitation ceases and a slight odour of bromine remains; the precipitated powder, which has a reddish tint arising from a decomposition-product, is collected, and freed from this impurity by distillation in a small retort; and the distillate, which solidifies in a crystalline mass, is recrystallised from boiling alcohol (Fritzsche).—3. An aqueous solution of hydrochlorate of bromaniline is mixed with aqueous bromine, and the violet-white precipitate is distilled with water, whereby snow-white crystals are obtained at first, but afterwards violet crystals which cannot be decolorised by recrystallisation from alcohol. (Hofmann.)

*Properties.*—Tribromaniline crystallised from hot alcohol forms colourless, shining, long, slender needles; but when solidified after fusion, it is of a crystalline texture, brittle and easily pulverised. Melts at 117° to a clear liquid; boils at about 300°; distils over unchanged (Fritzsche), and sublimes in radiating crystals having a silky lustre (Hofmann). It is insoluble in *water;* sparingly soluble in cold, easily in boiling *alcohol* and *ether*. It is not basic, and does not dissolve either in dilute acids or in alkalis. Strong boiling *nitric acid* decomposes it. Warm strong *sulphuric acid* dissolves it without decomposition, acquiring a purple colour from decomposition only when heated nearly to the boiling point. Strong *potash-ley* has no action on it, even at the boiling heat.

**Azobromophenylamine** or *Diazobromobenzene*, $C^6H^3BrN^2 = \left.\begin{matrix}(C^6HBrN''')'\\H^2\end{matrix}\right\}N^2.$ (Griess, Proc. Roy. Soc. 1864 [3] 695.)—The nitrate of this base is produced by the action of nitrous acid on an aqueous solution of nitrate of bromaniline or an ethereal solution of azobromodiphenyl-diamine, just in the same manner as azophenylamine is prepared from nitrate of aniline or from azodiphenyldiamine (p. 429). In the former case the nitrous acid gas must be passed very rapidly at first; otherwise azobromodiphenyldiamine will be formed, which is very difficult to convert into nitrate of azobromophenylamine in an aqueous solution. The product obtained by either process may be purified by repeated solution in alcohol and precipitation with ethers.

The concentrated aqueous solution of the nitrate treated with strong caustic potash, yields the compound $C^6H^3BrN^2.KHO$, from which the azobromophenylamine may be separated by dilute acetic acid in slender bright yellow needles. It may also be obtained as a bright yellow amorphous precipitate by adding potash to the aqueous solution of the nitrate. In either case it must be quickly removed from the mother-liquor and dried over oil of vitriol.

Azobromophenylamine is a very dangerous compound, the slightest pressure or even contact with a rough object causing it to go off in a fiery explosion, equalling, if not exceeding in violence that of azophenylamine. It is much more stable at ordinary temperatures than azophenylamine; nevertheless it does not long remain unchanged, and after being kept for some time, leaves a reddish-brown residue which no longer explodes even when heated, and appears to have lost all its nitrogen. *Ether* dissolves azobromophenylamine with evolution of gas, frequently violent enough to cause explosion. Azobromophenylamine when recently prepared dissolves in *potash* and in *mineral acids*.

Salts of Azobromophenylamine. These salts may be formed by direct combination of the base with acids, but more conveniently by methods similar to those already described for the preparation of salts of azophenylamine.

The *hydrobromate*, $C^6H^3BrN^2.HBr$, is obtained by decomposing a solution of the sulphate with bromide of barium, or by the action of an ethereal solution of bromine on an ethereal solution of azobromodiphenyldiamine:

$$\underset{\text{Azobromodiphenyl-diamine.}}{C^{12}H^9Br^2N^3} + Br^4 = \underset{\text{Hydrobromate of Azobromophenylamine.}}{C^6H^3BrN^2.HBr} + \underset{\text{Tribromaniline.}}{C^6H^4Br^3N} + HBr.$$

It forms white shining scales, very soluble in water, less soluble in alcohol, insoluble in ether. In the dry state it may be kept for a long time without decomposition. When heated, it explodes almost as violently as the nitrate. Its aqueous solution treated with moist chloride of silver yields the hydrochlorate.

The *bromoplatinate*, $2(C^6H^3BrN^2.HBr)Pt^{iv}Br^4$, is obtained by precipitation in ruby-red crystals; when heated with carbonate of sodium, it splits up as shown by the equation:

$$\underset{\text{Bromoplatinate.}}{2(C^6H^3BrN^2.HBr).PtBr^4} = \underset{\text{Dibromobenzene.}}{2C^6H^4Br^2} + Br^4 + N^4 + Pt.$$

*Perbromide of Azobromophenylammonium*, $C^6H^4BrN^2Br^3$, is obtained, by treating the hydrobromate, nitrate, or sulphate with excess of bromine-water, as an orange-coloured crystalline precipitate; sometimes also in the preparation of the hydrobromate from azobromodiphenyldiamine, in which case the hydrobromate may be dissolved out from it by washing with cold water.

The perbromide crystallises from solution in a small quantity of cold alcohol in orange-coloured monoclinic prisms, insoluble in water, freely soluble in warm, sparingly in cold alcohol, very sparingly in cold ether. When heated alone or with carbonate of sodium it is resolved into dibromobenzene, bromine and nitrogen:

$$C^6H^4BrN^2.Br^3 = C^6H^4Br^2 + Br^2 + N^2.$$

It is also converted into dibromobenzene by boiling its alcoholic solution. With aqueous *ammonia* it yields azobromophenylene-diamine, $\left.\begin{matrix}(C^6BrN''')''\\ H^4\end{matrix}\right\}N^3$.

$$C^6H^4BrN^2.Br^3 + 4NH^3 = C^6H^4BrN^3 + 3NH^4Br.$$

In like manner with ethylamine, phenylamine, &c., it yields ethyl- and phenyl-azobromo-phenylene-diamine, &c.

*Hydrochlorate of Azobromophenylamine*, $C^6H^3BrN^2.HCl$, is obtained by decomposing the aqueous hydrobromate with moist chloride of silver. The *chloroaurate*, $C^6H^3BrN^2.HCl.AuCl^3$, is precipitated by auric chloride from the aqueous nitrate as a yellow oil which soon solidifies to a crystalline mass. It is insoluble in water, but dissolves in warm alcohol, crystallising therefrom in small golden-yellow shining plates. It is decomposed by sulphydric acid in the same manner as the gold-salt of azophenylamine (p. 430). The *chloroplatinate*, $2(C^6H^3BrN^2.HCl)Pt^{iv}Cl^4$, is precipitated by platinic chloride from the nitrate or sulphate, in small yellow crystals which appear under the microscope as fractured plates and are almost insoluble in any neutral solvent. They are stable at 100°. Heated with carbonate of sodium it yields chlorobromobenzene according to the equation:

$$2(C^6H^3BrN^2.HCl).PtCl^4 = 2C^6H^4BrCl + Pt + Cl^4 + N^4.$$

*Nitrate*, $C^6H^3BrN^2.NHO^3$.—Prepared as above described (p. 436). Crystallises in pure white scales or regular rhombic plates, very soluble in water, sparingly soluble in strong alcohol, almost insoluble in ether. It explodes when heated, struck, or pressed, but not so violently as nitrate of azophenylamine. When boiled with *water* it is resolved into bromophenic acid, nitric acid, and free nitrogen:

$$C^6H^3BrN^2.NHO^3 + H^2O = C^6H^5BrO + NHO^3 + N^2.$$

Boiled with *alcohol*, it yields bromobenzene and probably bromodinitrophenic acid:

$$\underset{\text{Nitrate of Azobromophenylamine.}}{2(C^6H^4BrN^2.NHO^3)} + \underset{\text{Alcohol.}}{C^2H^6O} = \underset{\text{Bromobenzene.}}{C^6H^5Br} + \underset{\text{Bromodinitrophenic acid.}}{C^6H^3Br(NO^2)^2O} + \underset{\text{Aldehyde.}}{C^2H^4O}$$
$$+ H^2O + N^4.$$

With *ammonia*, it forms azodibromodiphenyldiamine, together with a yellow body:

$$2C^6H^4BrN^2 + NH^3 = C^{12}H^9Br^2N^3 + N^2.$$

The same compound is formed on adding a concentrated aqueous solution of the nitrate to an alcoholic solution of bromaniline:

$$C^6H^4BrN^2 + C^6H^6BrN = C^{12}H^9Br^2N^3;$$

With *aniline*, the nitrate yields azobromodiphenyldiamine:

$$C^6H^4BrN^2.NHO^3 + 2C^6H^7N = C^{12}H^{10}BrN^3 + C^6H^7N.NHO^3,$$

identical, or at least isomeric, with the product obtained by the action of bromaniline on nitrate of azophenylamine (p. 432).

The aqueous solution of the nitrate mixed with *oxybenzamic acid* yields azobromophenyl-oxybenzamic acid, $C^{13}H^{10}BrN^3O^2$, which crystallises from ether in small roundish lumps of small needles or plates, and in every other respect is similar to azophenyl-oxybenzamic acid (p. 433).

*Sulphate of Azobromophenylamine*, $C^6H^4BrN^2.SH^2O^4$, obtained by the action of sulphuric acid on the nitrate, crystallises in very fine colourless prisms, very soluble in water, sparingly soluble in alcohol, almost insoluble in ether. It is comparatively stable, and may be recrystallised from water, without the slightest decomposition, by evaporation over oil of vitriol. It explodes by heat and is decomposed by boiling *water*. When heated with *sulphuric acid*, it is converted into a sulpho-acid, probably disulphobromophenylenic acid, $C^6H^3Br.2SH^2O^4$.

COMPOUNDS OF AZOBROMOPHENYLAMINE WITH METALLIC HYDRATES.—The *potassium-compound*, $C^6H^4BrN^2.KHO$, is prepared and purified exactly like the corresponding compound of azophenylamine, from which it differs in being precipitated from its alcoholic solution by ether as a white gelatinous mass, and not in crystals.

The *silver-salt*, $C^6H^4BrN^2.AgHO$, is an almost insoluble precipitate, very similar to the corresponding compound of azophenylamine (p. 433).

**Azodibromophenylamine** or *Diazodibromobenzene*, $C^6H^3Br^2N^2$. (Griess, Phil. Trans. 1864 [3] 704).—The *nitrate* of this base is obtained by passing a rapid current of nitrous acid into aqueous nitrate of dibromaniline containing free nitric acid, then leaving the solution to evaporate spontaneously, dissolving the residue in weak alcohol, and precipitating with ether. It can be recrystallised from water or alcohol by evaporation below the boiling points of the respective solutions. The aqueous solution is remarkably stable, not being completely decomposed even by several hours boiling. The salt crystallises in fine white needles or elongated hexagonal plates. It does not detonate so violently as the nitrates of azophenylamine and azobromophenylamine.

The *perbromide*, $C^6H^3Br^2N^2.Br^3$, produced by adding bromine-water to the aqueous nitrate, is precipitated in long slender needles. By boiling with *alcohol*, it yields tribromobenzene, $C^6H^3Br^3$. Aqueous *ammonia* converts it into azodibromophenylene-diamine, $C^6H^3Br^2N^3 = \left.\begin{matrix}(C^6HN''')''\\ Br^2\\ H^2\end{matrix}\right\}N^2.$

The chloroplatinate, $2(C^6H^3Br^2N^2.HCl)Pt^{iv}Cl^4$, separates on adding platinic chloride to the hydrochlorate, in small orange-coloured oval plates, sparingly soluble in water.

### 3. *Chlorophenylamines.*

**Monochlorophenylamine,** or **Chloraniline,** $C^6H^6ClN = \left.\begin{matrix}C^6H^4Cl\\ H^2\end{matrix}\right\}N$.—Of this base there are also two modifications, analogous to α- and β-bromaniline, exhibiting corresponding difference of physical properties and produced by analogous reactions. The first was discovered by Hofmann (Ann. Ch. Pharm. liii. 1); the second by Griess (Phil. Trans. 1864 [3] 713).

*Preparation of α-chloraniline.*—1. Chlorisatin is distilled with potash-ley or hydrate of potassium, till the residue has become solid, gives off ammonia together with the hydrogen, and yields a blue sublimate and a brown oil which no longer solidifies on cooling. The solidified oil which first passed over is then collected on a filter, freed from ammonia by water, and crystallised from boiling alcohol (Hofmann).—2. Chlorophenylacetamide, $(C^6H^4Cl)(C^2H^3O)HN$ (obtained by the action of chlorine on phenylacetamide), yields by distillation with potash, a large quantity of chloraniline (Mills).

3. By the action of sulphide of ammonium on β-nitrochlorobenzene (p. 416) (Griess).—β-chloraniline is obtained by the action of sulphide of ammonium on α-nitrochlorobenzene. (Griess.)

*Properties.*—Alpha-chloraniline crystallises in octahedrons having a diamond lustre, heavier than water, melting between 64° and 65°, into a yellow oil which solidifies at 57° in large octahedrons. It evaporates even at ordinary temperatures, so that hydrochloric acid held over it produces fumes; may be easily distilled with water; boils by itself at a temperature above 200°, and with some decomposition, so that, together with the oil, the above-mentioned blue product passes over. It has an agreeable vinous odour and an aromatic burning taste like that of aniline; does not act upon red litmus or turmeric, but turns dahlia flowers green.—β-chloraniline is an oil which remains liquid at common temperatures.

Chloraniline (α or β) dissolves sparingly in water, the boiling solution becoming milky and depositing octahedral crystals in cooling; soluble in *wood-spirit*, in *alcohol* (readily when hot), in ether (which abstracts it from the aqueous solution), in acetone, and easily in sulphide of carbon; also in *oils*, both fixed and volatile. The hot saturated aqueous solution mixed with tincture of galls forms yellow flakes on cooling.

*Decompositions.*—1. Chloraniline *burns* with a bright, strongly fuliginous flame, having a bright green border.—2. *Chlorine* together with water, converts chloraniline, partly into trichloraniline, partly into trichlorophenic acid:

$$C^6H^6ClN \quad + \quad Cl^4 \quad = \quad C^6H^4Cl^3N \quad + \quad 2HCl\,;$$

and:

$$[C^6H^6ClN \quad + \quad Cl^4 \quad + \quad H^2O \quad = \quad C^6H^3Cl^3O \quad + \quad HCl \quad + \quad NH^4Cl.$$

3. *Bromine*, either anhydrous or hydrated, decomposes chloraniline, with great evolution of heat, forming dibromochloraniline and hydrobromic acid:

$$C^6H^6ClN \quad + \quad Br^4 \quad = \quad C^6H^4Br^2ClN \quad + \quad 2HBr.$$

4. Heated with strong *nitric acid*, it begins to boil and continues boiling even after removal from the fire; gives off nitrous acid; and yields, first, a dark red, then a black opaque liquid, and afterwards, as the heating is continued, a clear scarlet solution, which does not precipitate nitrate of silver, and on cooling, yield, sometimes golden yellow needles resembling picric acid, and probably consisting of dinitrochlorophenic acid $C^6H^3(NO^2)^2ClO$, sometimes a resin, which is precipitated by water in yellow flakes, and dissolves with deep yellow colour in alkalis, alcohol and ether; the solution of this resin in alkalis is precipitated by acids, and its ammoniacal solution, when freed from excess of ammonia by boiling, precipitates silver-solution reddish-yellow, sometimes also in yellow crystalline spangles.—5. The aqueous solution of chloraniline acquires a very faint violet tint when treated with *chloride of lime.*—6. With *chlorate of potassium* and *hydrochloric acid*, chloraniline forms a violet-red, then a turbid brown, and ultimately a colourless liquid, which at first deposits crystalline perchloroquinone, together with tri- and penta-chlorophenic acid in the form of a brown viscid substance soluble in alcohol, but after decoloration contains nothing but perchloroquinone and sal-ammoniac; the same reaction therefore as with aniline:

$$C^6H^6ClN \quad + \quad Cl^4 \quad + \quad H^2O \quad = \quad \underset{\text{Trichlorophenic acid.}}{C^6H^3Cl^3O} \quad + \quad NH^4Cl \quad + \quad HCl\,;$$

further:

$$C^6H^6ClN \quad + \quad Cl^8 \quad + \quad H^2O \quad = \quad \underset{\text{Pentachlorophenic acid.}}{C^6HCl^5O} \quad + \quad NH^4Cl \quad + \quad 3HCl\,;$$

and:

$$C^6H^6ClN \quad + \quad Cl^6 \quad + \quad O^2 \quad = \quad \underset{\text{Perchloroquinone.}}{C^6Cl^4O^2} \quad + \quad NH^4Cl \quad + \quad 2HCl.$$

7. The crystals, immersed in aqueous *chromic acid*, turn brown and become resinised; the dry mixture takes fire at the melting point of chloraniline.—8. Aqueous chloraniline imparts to *ferric salts* a green colour by deoxidation, and on boiling, deposits a blackish-violet product soluble in alcohol.—9. When the vapour is passed over *lime* at a low red heat, aniline and ammonia pass over, a large quantity of charcoal is separated, and chloride of calcium is formed:

$$2C^6H^6ClN \quad + \quad CaO \quad = \quad C^6H^7N \quad + \quad C^6 \quad + \quad CaCl^2 \quad + \quad NH^3 \quad + \quad H^2O.$$

10. Melted *potassium* immersed in the vapour of chloraniline, forms chloride and cyanide of potassium, with vivid incandescence and separation of a large quantity of charcoal. On the other hand, *potassium-amalgam*, with water, reduces chloraniline to aniline. (Hofmann, Ann. Ch. Pharm. lxvii. 76.)

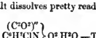
Chloraniline is not so strong a base as aniline; it does not precipitate sulphate of aluminium or ferrous, ferric, or zinc salts; it expels ammonia from ammoniacal salts when heated with them, but is itself precipitated by ammonia from its hydrochloric acid solution, and neutralises acids but imperfectly. Its salts mostly crystallise readily, and, in consequence of their sparing solubility, are generally precipitated on mixing an acid with alcoholic chloraniline, in the form of a crystalline pulp, which may be purified by recrystallisation from boiling water or alcohol. They are mostly colourless or yellowish in mass, and violet when they contain excess of acid; they redden litmus even when completely saturated with the base. Like the aniline-salts, they impart a deep yellow colour to firwood and elder-pith, but with chloride of lime they assume only a very faint violet tint, changing afterwards to orange-yellow. They are immediately decomposed by alkalis; also by alkaline carbonates. with evolution of carbonic acid, inasmuch as that acid does not combine with chloraniline.

*Hydrochlorate of Chloraniline*, $C^6H^6ClN.HCl$.—Hydrochloric acid saturated at a boiling heat with chloraniline, yields on cooling large crystals, which may be still further developed by slow evaporation of their aqueous solution over oil of vitriol. They have the same form as hydrochlorate of bromaniline. They are permanent in the air, become opaque when warmed, and sublime undecomposed when cautiously raised to a higher temperature, whereas sudden heating decomposes them, with formation of a violet vapour. The *chloroplatinate* of *α-chloraniline*, $2C^6H^6ClN.H^2Cl^2.Pt^{iv}Cl^4$, separates on mixing a cold solution of the hydrochlorate with platinic chloride, as a beautiful orange-coloured precipitate, and a hot mixture of the two salts solidifies on cooling to a pulp of crystalline laminæ; the salt, when exposed to light, becomes covered with a violet film. (Hofmann.)

*Chloroplatinate of β-chloraniline* forms yellow crystals differing considerably in form and solubility from those of the α-salt. (Griess.)

The aqueous solution of *chloraniline* forms a red-brown precipitate with *trichloride of gold* and an orange-coloured precipitate with *chloride of palladium*. The cold aqueous solution of chloraniline immediately forms a white precipitate with *mercuric chloride*; the hot mixture solidifies after a while into a magma of needle-shaped crystals. A mixture of the aqueous solutions of chloraniline and *stannous chloride* quickly solidifies to a silver-shining crystalline mass.

*Nitrate of Chloraniline.*—The solution of chloraniline in warm dilute nitric acid becomes filled, as it cools, with large crystalline laminæ, mostly of a reddish colour. These crystals, which cannot be sublimed without decomposition, melt when heated in a tube, into a dark-coloured mass, which dissolves with splendid violet colour in alcohol, while part of the salt crystallises out undecomposed. The salt dissolves pretty readily in water and alcohol.

*Oxalate* (*acid*) *of Chloraniline*, $C^6H^6ClN.C^2H^2O^4.H^2O$ = 

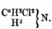
$$\left.\begin{matrix}(C^2O^2)''\\ C^6H^7ClN\\ H\end{matrix}\right\}O^2.H^2O$$

.—The solution of chloraniline in the warm aqueous acid yields, on cooling, crystals, which, when recrystallised from boiling water, form prisms made up of smaller ones joined together. They have a sweetish burning taste, and dissolve sparingly in water and alcohol; the aqueous solution becomes coloured on exposure to the air and deposits a red powder. It does not appear possible to obtain a neutral oxalate of chloraniline in the crystalline state.

*Phosphate of Chloraniline.*—Alcoholic chloraniline solidifies with aqueous phosphoric acid into a magma of crystalline laminæ, which dissolve pretty readily in water and alcohol.

*Sulphate of Chloraniline*, $(C^6H^6ClN)^2.H^2SO^1 = (C^6H^7ClN)^2SO^4$.—The white crystalline magma, into which alcoholic chloraniline solidifies when mixed with a small quantity of acid, yields, when dissolved in boiling water, confused violet-white laminæ, and when dissolved in boiling alcohol, silvery needles arranged in stellate groups. The crystals when heated give off a small quantity of chloraniline, then blacken, and evolve sulphurous acid. They are less soluble in alcohol than in water.

Aqueous *sulphate of copper*, which is not precipitated by aqueous chloraniline, soon becomes decolorised by boiling with crystalline chloraniline, and deposits a bronze-coloured crystalline mass, which is insoluble in water, and dissolves but sparingly in boiling alcohol, whence it crystallises in spangles on cooling; probably a double sulphate of chloraniline and copper.

**Dichloraniline,** $C^6H^5Cl^2N$ = 

$$\left.\begin{matrix}C^6H^3Cl^2\\ H^2\end{matrix}\right\}N.$$

(Hofmann, Ann. Ch. Pharm. liii. 33 and 57.—Griess, *ibid.* cxxi. 257.)—Hofmann, by distilling dichlorisatin still containing monochlorisatin with potash, obtained long prisms consisting of dichloraniline mixed with a small quantity of the monochlorinated base. Dichloraniline is however more easily prepared by passing chlorine into phenylacetamide till the mass becomes rather soft, and distilling the resulting dichlorophenyl-acetamide with potash. It may be purified in the same manner as dibromaniline (Griess). It crystallises in white needles nearly insoluble in *water*, easily soluble in *alcohol* and *ether*. The *platinum-salt*, $2C^6H^5Cl^2N.H^2Cl^2.Pt^{iv}Cl^4$, forms yellow needles easily decomposed by hot water. (Griess.)

**Trichlorophenylamine** or **Trichloraniline.** (Erdmann, J. pr. Chem. xix. 331, xxv. 472.—Hofmann, Ann. Ch. Pharm. liii. 35.)—This compound (the *chlorindatmit* of Erdmann, who, however, overlooked the nitrogen contained in it), distils over, together with trichlorophenic acid, in the preparation of the latter by the action of chlorine on indigo (p. 393) (Erdmann). It is also produced, together with trichlorophenic acid, by the action of chlorine on aniline or monochloraniline; and when this mixture is distilled with potash-ley into a well-cooled receiver, the trichloraniline passes over in needles floating on the water, and as an oil which solidifies in the crystalline form. (Hofmann.)

It crystallises in delicate, white, very fragile needles and laminæ, easily melting into a colourless oil which crystallises on cooling; it is volatile and neutral, and has a peculiar odour. (Erdmann, Hofmann.)

It dissolves sparingly in cold, more freely in boiling *water;* readily in *alcohol* and *ether;* does not combine either with *acids* or with *alkalis.*

With *nitric acid* it evolves nitrous fumes and forms a yellow solution which turns red when mixed with potash (Erdmann).—The vapour passed over heated soda-lime, yields a large quantity of ammonia, and when passed over melted potassium, it yields a large quantity of cyanide of potassium (Hofmann).—It is not decomposed by distillation with potash-ley. (Erdmann, Hofmann.)

**Chlorodibromaniline**, $C^6H^4ClBr^2N = \left.\begin{matrix}C^6H^2ClBr^2\\H^2\end{matrix}\right\}N.$ (Hofmann, Ann. Ch. Pharm. liii. 38.)

*Preparation.*—1. Crystalline chloraniline treated with anhydrous bromine becomes very hot and gives off a large quantity of hydrobromic acid, assumes a violet colour, and is converted, after it no longer absorbs bromine, even when melted, into chlorodibromaniline, which solidifies on cooling, and must be washed with cold water and recrystallised from alcohol.—2. When the whitish precipitate which bromine-water forms in an aqueous solution of a salt of chloraniline, is dissolved in hot alcohol, a pale violet solution is obtained which yields needle-shaped crystals.

*Properties.*—White prisms, often with a tinge of red. They melt in hot water, forming a brown oil, which volatilises with the vapour of boiling water and sublimes in shining needles. Insoluble in water, soluble in alcohol and ether; decomposed by strong nitric acid.

It does not exhibit the characters of a salifiable base; it dissolves indeed, with violet colour, in *oil of vitriol*, but is precipitated therefrom by water; dissolves also in hot strong *hydrochloric acid*, but the greater part of it separates on cooling, and the rest on addition of water.

It dissolves without alteration in warm *ammonia* and *potash;* does not form compounds with chloride of mercury or tetrachloride of platinum.

**Azochlorophenylamine** or *Diazochlorobenzene*, $C^6H^3ClN^2 = \left.\begin{matrix}(C^6HClN'')'\\H^2\end{matrix}\right\}N.$ (Griess, Phil. Trans. 1864 [3] 705.)—The *nitrate* of this base, prepared like that of azobromophenylamine (p. 437), crystallises in small white plates which, when boiled with water, yield chlorophenol.

The *perbromide*, $C^6H^4ClN^2.Br^3$, forms yellow prisms which are decomposed by boiling alcohol, yielding bromochlorobenzene, isomeric or identical with that obtained from the chloroplatinate of azobromophenylamine (p. 436). When decomposed by ammonia, it yields azochlorophenylene-diamine or diazochlorobenzoylimide, $C^6H^4ClN^3$.

The *chloroplatinate*, $2(C^6H^3ClN^2.HCl.)Pt^{iv}Cl^4$, forms fine yellow needles which, when heated with carbonate of sodium, yield dichlorobenzene.

Azochlorophenylamine precipitated by acetic acid from its compound with hydrate of potassium, is a lemon-yellow explosive powder.

**Azodichlorophenylamine** or *Diazochlorobenenzene*, $C^6H^2Cl^2N^2$. (Griess, *loc. cit.*)—The *nitrate* forms white plates. The *perbromide*, $C^6H^3Cl^2N^2.Br^3$, crystallises in yellow prisms; the *chloroplatinate*, $2(C^6H^2Cl^2N^2.HCl).Pb^{iv}Cl^4$, in small, yellow, very brilliant plates.

### 4. *Cyanophenylamines.*

**Cyanilide** or **Cyaniline**, $C^7H^6N^2 = \left.\begin{matrix}C^6H^4Cy\\H^2\end{matrix}\right\}N.$ (Cahours and Cloez, Compt. rend. xxxviii. 38, 355.)—When pure and very dry gaseous chloride of cyanogen is passed into a solution of aniline in anhydrous ether cooled with ice, a crystalline deposit is formed, consisting of hydrochlorate of aniline, which continually increases; and the filtrate evaporated over the water-bath, leaves cyanilide in the form of a viscid mass which solidifies as it cools. It is a reddish substance resembling colophony in friability, conchoïdal fracture and translucence. It is completely decomposed by heat, yielding various products. Its alcoholic solution mixed with hydrochlorate of aniline and evaporated for some time over the water-bath, yields crystallised hydrochlorate of melaniline:

$$C^6H^7N \quad + \quad C^7H^6N^2 \quad = \quad \underset{\text{Melaniline.}}{C^{13}H^{13}N^3.}$$

Cyanilide is insoluble in water, but dissolves readily in alcohol and ether. *Water* added to the alcoholic or ethereal solution, immediately separates a viscous substance which gradually becomes crystalline.

*Compound of Cyanilide with Chloride of Cyanogen:* CHLOROCYANILIDE, $C^{15}H^{12}N^5Cl = 2C^7H^6N^2.CNCl$. (Laurent, Ann. Ch. Phys. [3] xxii. 97.)—When solid chloride of cyanogen in the state of powder is gradually introduced into a flask containing aniline dissolved in lukewarm water and the requisite quantity of alcohol, chlorocyanilide falls down as a white powder, which must be washed with water and alcohol successively, after the liquid which contains the hydrochlorate of aniline has been decanted:

$$4C^6H^7N \quad + \quad C^3N^3Cl^3 \quad = \quad C^{15}H^{12}N^5Cl \quad + \quad 2(C^6H^7N.HCl).$$

Its formation is similar therefore to that of chlorocyanamide, $2CH^2N^2.CNCl$, by the action of ammonia on solid chloride of cyanogen.

Chlorocyanilide crystallises from alcohol on cooling in white, highly lustrous, somewhat elongated laminæ, and after fusion in radiating needles. Not volatile without decomposition.

When heated somewhat above its melting point, it gives off 11·8 per cent. of hydrochloric acid, becoming less fluid, and ultimately leaves a greenish, transparent, vesicular residue, containing $C^{15}H^{11}N^5$. It dissolves slowly in boiling *potash*, and on neutralising the cooled solution with nitric acid, a white flocculent precipitate is obtained, which is insoluble in ammonia, but dissolves in hot weak nitric acid, separates in the form of a jelly on cooling, and contains 62·6 per cent. carbon, and 4·6 hydrogen (Laurent). Laurent regards this substance as phenyl-ammeline, $C^{15}N^5H^{13}O = C^3H^3(C^6H^5)^2N^5O$ (which however requires 2 per cent. more carbon), and represents its formula by the equation:

$$C^{15}H^{12}N^5Cl \quad + \quad KHO \quad = \quad C^{15}H^{13}N^5O \quad + \quad KCl.$$

The subject requires further investigation.

**Cyananiline,** $C^7H^7N^2$ or rather $C^{14}H^{14}N^4 = C^{12}H^{14}N^2.Cy^2$. (Hofmann, Chem. Soc. Qu. J. i. 160; ii. 300; Ann. Ch. Pharm. lxvi. 129; lxxiii. 180.)—This substance, though not a substitution-product of aniline, but a compound of aniline and cyanogen formed by direct union, without elimination of hydrogen, may be conveniently described in this place.

To prepare it, cyanogen gas is passed through a solution of aniline in a six-fold quantity of alcohol, till the liquid smells strongly of it, but not longer; and the resulting crystals are freed from the mother-liquor, which colours them reddish-yellow, either by repeated washing with cold alcohol, or by washing them twice with that liquid, and subsequently dissolving them in dilute sulphuric acid, filtering from a red crystalline powder, precipitating the pale yellow filtrate by ammonia, and crystallising the pale yellow pulverulent precipitate once, twice or three times from a large quantity of boiling alcohol, till colourless laminæ are obtained.

Cyananiline crystallises in colourless, silvery, iridescent laminæ, which do not volatilise without decomposition, even in company with vapour of water; they melt between 210° and 220°, and solidify in the crystalline form on cooling; they are heavier than water; inodorous, tasteless and neutral. The acid solutions of this base do not colour firwood yellow; neither do they turn blue in contact with chloride of lime, or give the precipitates of aniline with chromic acid. It is insoluble in *water*, and only slightly soluble in *sulphide of carbon*, *wood-spirit*, *alcohol*, *ether*, *benzene* and *oils*, whether fixed or volatile.

*Decompositions.*—1. Cyananiline at a temperature a little above its melting point, turns brown, chars, and gives off aniline together with hydrocyanate of ammonia.—2. *Bromine* becomes strongly heated in contact with cyananiline, and perhaps forms at first, bromocyananiline, which however is ultimately converted into tribromaniline.—3. The violet solution of cyananiline in *oil of vitriol* gives off, when slightly heated, a mixture of carbonic anhydride and carbonic oxide, which latter is more and more replaced by sulphurous acid as the heat increases; and the liquid on cooling solidifies in a crystalline mass consisting of sulphate of ammonium and phenyl-sulphamic acid:

$$C^{14}H^{14}N^4 + 3H^2SO^4 + H^2O = 2\left[\left.\begin{matrix}H.C^6H^5\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}\right] + (NH^4)^2SO^4 + CO + CO^2.$$

4. The solution in dilute *hydrochloric* (or dilute sulphuric acid) soon assumes a deep yellow colour, and when evaporated over the water-bath, gives off an odour of phenylic cyanate, $C^6H^5.CNO$ (ii. 196), and leaves a white crystalline mass, from which sal-ammoniac and hydrochlorate of aniline are extracted by cold water, and afterwards oxamide and phenyl-oxamide by boiling water, whilst diphenyl-oxamide is left undissolved in quantity equal to that of the oxamide and the phenyl-oxamide. In this case, two decompositions appear to take place simultaneously:

$$(1)\ C^{14}H^{14}N^4 + 2H^2O + 2HCl = 2NH^4Cl + \left.\begin{matrix}(C^2O^2)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2.$$

Diphenyloxamide.

$$(2)\ C^{14}H^{14}N^4 + 2H^2O + 2HCl = \left.\begin{matrix}(C^2O^2)''\\H^4\end{matrix}\right\}N^2 + 2C^6H^8NCl.$$

Oxamide. Hydrochlorate of aniline.

At the moment of formation (but not afterwards) the oxamide and diphenyl-oxamide are partly converted into phenyloxamide:

$$C^2H^4N^2O^2 + C^{14}H^{12}N^2O^2 = 2C^8H^8N^2O^2.$$

Cold dilute acids gradually eliminate aniline and give off the odour of phenylic cyanate. —5. Cyananiline is not altered by boiling aqueous or alcoholic potash, but by *potassic hydrate* in the state of fusion, it is converted into ammonia, aniline, hydrogen gas, and carbonate of potassium:

$$C^{14}H^{14}N^4 + 4KHO + 2H^2O = 2NH^3 + 2C^6H^7N + H^2 + 2K^2CO^3.$$

SALTS OF CYANANILINE.—These salts are formed by direct combination of the acid and base, and must be brought to the solid state as quickly as possible, before they decompose. They are not produced by passing cyanogen gas through alcoholic solutions of aniline-salts. According to the formula $C^{14}H^{14}N^4$, they must be regarded as diacid salts.

*Hydrobromate*, $C^{14}H^{14}N^4.2HBr$.—Cyaniline is dissolved in boiling dilute hydrobromic acid, and the filtrate immediately mixed with an equal quantity of concentrated hydrobromic acid, which separates crystals, to be washed, first with concentrated hydrobromic acid, then with ether. The salt is very much like the following.

*Hydrochlorate*, $C^{14}H^{14}N^4.2HCl$.—The yellow solution of cyananiline in boiling dilute hydrochloric acid, is filtered hot and immediately mixed with an equal quantity of fuming hydrochloric acid, which decolorises it, and soon causes the separation of a large quantity of colourless crystals, which must be washed with hydrochloric acid and then with ether. These crystals have a very sweet taste, and are permanent when dry, but decompose in the moist state, becoming at the same time insoluble in water. Their aqueous solution yields by evaporation, the same products of decomposition as the direct solution of cyananiline in dilute hydrochloric acid (*vid. sup.*). Aniline added to the aqueous solution of the crystals, precipitates the cyananiline as the weaker base, and acids throw down the crystals in their original state. The crystals dissolve with great facility in water and in alcohol. The *chloro-aurate*, $C^{14}H^{14}N^4.2(HCl.AuCl^3)$, is an orange-coloured precipitate obtained by adding auric chloride to a solution of cyananiline in alcohol or hydrochloric acid. The *chloroplatinate*, $C^{14}H^{14}N^4.2HCl.Pt^{iv}Cl^4$, is precipitated on mixing a moderately concentrated solution of cyananiline in hydrochloric acid saturated at the boiling heat, with a concentrated solution of platinic chloride, and leaving the liquid to cool. It forms beautiful orange-coloured needles which are soluble in water and alcohol, but cannot be recrystallised from those liquids, the solutions yielding nothing but chloroplatinate of aniline and chloroplatinate of ammonium.

*Hydriodate of Cyananiline* resembles the hydrochlorate and hydrobromate, but decomposes quickly on exposure to the air, with separation of iodine.

*Nitrate*, $C^{14}H^{14}N^4.2HNO^3$.—Cyananiline dissolves easily in boiling dilute nitric acid, and the solution on cooling deposits the nitrate in white needles which may be recrystallised from boiling water. It is but slightly soluble in cold water, still less in alcohol and ether. It forms a crystallisable double salt with nitrate of silver.

The *oxalate* and *sulphate* are very soluble, and their solutions decompose during evaporation.

### 5. *Iodophenylamines.*

**Mono-iodophenylamine** or **Iodaniline,** $C^6H^6IN = \left.\begin{matrix}C^6H^4I\\H^2\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. lxvii. 64.)—To prepare this compound, 1½ pt. of iodine is gradually dissolved in 1 pt. of aniline; the solution is mixed with hydrochloric acid of specific gravity 1·11 (a stronger acid would separate hydrochlorate of aniline); the solution of hydrochlorate of aniline, hydriodic acid, &c., is separated by filtration from the precipitated and still strongly coloured hydrochlorate of iodaniline, which is sparingly soluble in water; the precipitate is washed several times with hydrochloric acid, and crystallised several times from boiling water, at last after boiling with animal charcoal, till the crystals, which are at first ruby-coloured and contain free iodine, together with a brown induretted decomposition-product of aniline, are completely decolorised; and the iodaniline is precipitated from their aqueous solution by ammonia, as a white crystalline powder, which—in order to free it from any of the yellowish decomposition-product and phosphate of calcium from the animal charcoal, that may still adhere to it—is dissolved in alcohol, filtered from the yellowish product, and precipitated by water in the form of a white crystalline mass. The liquid filtered therefrom yields by evaporation yellowish oily drops which crystallise on cooling.

*Properties.*—White crystalline powder, which crystallises from solution in prisms and needles, never in octahedrons; the mass solidified from cooling also never exhibits the cleavage-faces of the octahedron. It is heavier than water. Melts at 60°, forming a yellowish oil, and at the moment of solidification, shows a temperature of 51°, but sometimes remains liquid even at the ordinary temperature, in which case, contact with a glass rod often causes it to solidify suddenly in a crystalline mass. When evaporated at a rather strong heat, it volatilises undecomposed, and easily distils over even with vapour of water. It has a vinous odour and a burning aromatic taste, no action on vegetable colours. Like aniline, it imparts a deep yellow colour to firwood and elder-pith; but chloride of lime colours it, not violet but reddish. The vapour burns with a bright sooty flame.

Iodaniline dissolves very sparingly in cold *water*, and crystallises from boiling water in interlaced hairs. It dissolves in *sulphide of carbon*, also in *alcohol, ether, wood-spirit, acetone*, and *oils* both fixed and volatile.

*Decompositions.*—1. In contact with the *air*, iodaniline becomes quickly covered with a brown, metallically lustrous film, and gradually assumes a black colour extending throughout the whole mass.—2. *Chlorine* decomposes iodaniline into trichloraniline, trichlorophenic acid (as with aniline, p. 424), and chloride of iodine.—3. With *bromine*, alcoholic iodaniline solidifies in the form of crystalline tribromaniline, while all the iodine is set free as bromide of iodine.—4. *Chlorate of potassium* with *hydrochloric acid* forms, as with aniline, trichlorophenic acid and perchloroquinone.—5. With strong boiling *nitric acid*, iodaniline forms, with brisk action and evolution of iodine-vapour, a solution from which picric acid crystallises on cooling.—6. Crystallised *chromic acid* decomposes iodaniline with violence, but does not set it on fire.—7. Gently heated *potassium* decomposes iodaniline with violence, forming iodide and cyanide of potassium.—*Potassium-amalgam* introduced into aqueous nitrate of iodaniline, immediately forms iodide of potassium, and reproduces a small quantity of aniline, whilst the greater portion is converted into a yellow crystalline substance having an aromatic odour. *Zinc* immersed in iodaniline supersaturated with sulphuric acid, eliminates iodine and aniline, so that after a few minutes the liquid forms a blue colour with starch, and after saturation with potash, gives up aniline to ether.—8. When *chloride of cyanogen* is passed through iodaniline dissolved in ether, hydrochlorate of iodaniline is first precipitated but afterwards disappears, and the iodaniline is converted into a transparent, slowly crystallising resin, which is a mixture of hydrochlorate of di-iodomelaniline and iodophenyl-carbamide. Formation of hydrochlorate of di-iodomelaniline:

$$2C^6H^6NI + CNCl = C^{13}H^{11}I^2N^3.HCl.$$

Formation of iodophenylcarbamide and hydrochlorate of iodaniline:

$$2C^6H^6NI + CNCl + H^2O = (CO)''(C^6H^4I)H^3N^2 + C^6H^6IN.HCl.$$

Salts of Iodaniline.—These salts crystallise with the same facility as the aniline salts, but are less soluble. Iodaniline is a weaker base than aniline, and is separated by the latter from the solutions of its salts. It precipitates the salts of aluminium, but does not decompose ferric or zinc salts. With sulphate of copper it forms a yellow precipitate.

*Hydrobromate of Iodaniline* exactly resembles the hydrochlorate.

The *hydrochlorate*, $C^6H^6IN.HCl$, is sparingly soluble in cold water, and its aqueous solution is almost entirely precipitated by hydrochloric acid. It crystallises from boiling water in large thin laminæ or needles soluble in alcohol, insoluble in ether. The *chloroaurate* is an unstable scarlet precipitate formed on mixing the solutions of auric chloride and hydrochlorate of iodaniline. The *chloroplatinate*, $2C^6H^6IN.H^2Cl^2.Pt^{iv}Cl^4$, is an orange-coloured crystalline precipitate.

*Hydriodate of Iodaniline* forms a radiate mass much more soluble than the hydrobromate and hydrochlorate, and easily decomposible.

The *nitrate* crystallises from water in beautiful capillary needles of great length. It is more soluble than the preceding salts, especially in boiling water; very soluble also in alcohol and ether. Its solution is not precipitated by nitrate of silver.

The *oxalate*, $2C^6H^7IN.C^2H^2O^4 = (C^2O^2)''(C^6H^7IN)^2O^2$, crystallises in long flattened needles, sparingly soluble in water and in alcohol, insoluble in ether.

The *sulphate*, $2C^6H^6IN.SH^2O^4 = (C^6H^7IN)^2SO^4$, crystallises in shining scales. The aqueous solution appears to be decomposed by boiling; at all events, on attempting to recrystallise it after boiling, a portion of the salt always remains insoluble.

**Azo-iodophenylamine.** $C^6H^3IN^2 = \left.\begin{matrix}(C^6HIN''')' \\ H^2\end{matrix}\right\}N$. *Diazo-iodobenzol.* (Griess, Phil. Trans. 1864 [3] 706.)—This base and its salts are obtained by processes exactly similar to those employed for the preparation of the corresponding bromine-compounds (p. 436). Azoiodophenylamine in the free state is a yellow explosive precipitate. The *nitrate*, $C^6H^3IN^2.NHO^3$, crystallises in white prisms or needles, very soluble in water.—The *sulphate*, $C^6H^3IN^2.SH^2O^4$, in small plates easily soluble in water, sparingly soluble in alcohol.—The *chloroplatinate*, $(C^6H^3IN^2.HCl).Pt^{iv}Cl^4$, in bright yellow clusters of needles.—The *perbromide of azo-iodophenylammonium*, $C^6H^4IN^2.Br^3$, forms small yellow plates. With boiling alcohol it yields bromo-iodobenzene, $C^6H^4BrI$; and with aqueous ammonia it forms azo-iodophenylene-diamine, $\left.\begin{matrix}(C^6IN''')'' \\ H^4\end{matrix}\right\}N^2$, or diazo-iodobenzolimide, $\left.\begin{matrix}(C^6H^3IN^2)'' \\ H\end{matrix}\right\}N$.

### 6. *Nitrophenylamines.*

**Mononitrophenylamine** or **Nitraniline.** $C^6H^6(NO^2)N = \left.\begin{matrix}C^6H^4(NO^2) \\ H^2\end{matrix}\right\}N$.—(Hofmann and Muspratt, Ann. Ch. Pharm. lvii. 204.—E. Arppe, *ibid.* xc. 147; xciii. 157).—Of this base there are two isomeric modifications, the one called alpha-nitraniline (or by Arppe, *paranitraniline*), obtained by reducing dinitrobenzene with sulphydric acid (Hofmann and Muspratt); the other called beta-nitraniline* (*nitraniline* of Arppe), produced by the decomposition of nitro-phenyl-paratartrimide (Arppe), or of nitrophenyl-acetamide or nitrophenyl-succinamide under the influence of alkalis (Hofmann, Proc. Roy. Soc. x. 589; xii. 639):

$$\underset{\text{Dinitrobenzene.}}{C^6H^4(NO^2)^2} + 3H^2S = \underset{\text{Nitraniline.}}{C^6H^6(NO^2)N} + 2H^2O + S^3.$$

$$\underset{\text{Nitrophenyl-pyrotartrimide.}}{\left.\begin{matrix}C^6H^4(NO^2) \\ (C^5H^6O^2)''\end{matrix}\right\}N} + H^2O = \underset{\text{Nitrophenyl-pyrotartramic acid.}}{\left.\begin{matrix}H.C^6H^4(NO^2) \\ (C^5H^6O^2)'' \\ H\end{matrix}\right\}\begin{matrix}N \\ O\end{matrix}}.$$

$$\underset{\text{Nitrophenyl-pyrotartramic acid.}}{\left.\begin{matrix}H.C^6H^4(NO^2) \\ (C^5H^6O^2)'' \\ H\end{matrix}\right\}\begin{matrix}N \\ O\end{matrix}} + H^2O = \underset{\text{Nitraniline.}}{\left.\begin{matrix}C^6H^4(NO^2) \\ H^2\end{matrix}\right\}N} + \underset{\text{Pyrotartaric acid.}}{\left.\begin{matrix}(C^5H^6O^2)'' \\ H^2\end{matrix}\right\}O^2}.$$

$$\underset{\text{Nitrophenyl-acetamide.}}{\left.\begin{matrix}C^6H^4(NO^2) \\ C^2H^3O \\ H\end{matrix}\right\}N} + H^2O = \underset{\text{Nitraniline.}}{\left.\begin{matrix}C^6H^4(NO^2) \\ H^2\end{matrix}\right\}N} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}C^2H^3O \\ H\end{matrix}\right\}O}.$$

α-nitraniline was the first instance discovered of a basic substance containing the elements of nitric peroxide.

*Preparation.*—1. Of *α-nitraniline.*—The aqueous solution of dinitrobenzene is saturated with ammoniacal gas; sulphuretted hydrogen is passed through the blood-red solution, till the liquid is saturated with it and only a slight deposition of sulphur takes place; and the solution is then mixed with hydrochloric acid and evaporated, whereupon an additional quantity of sulphur separates, together with undecomposed dinitrobenzene. The filtrate is then mixed with potash, which precipitates a brown adhesive resin; this resin is freed from potash by washing with cold water, and then dissolved in boiling water; the orange-yellow solution is filtered to separate a small quantity of undissolved brown resin; and the needles of α-nitraniline which separate on cooling, are purified by recrystallisation from hot water (Hofmann and Muspratt). Arppe further purifies the crystals with animal charcoal.

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* The meaning here assigned to the terms α- and β-nitraniline is the same as that originally given by Hofmann, and adopted in most works on Chemistry (Gmelin's *Handbook*, Gerhardt's *Traité de Chimie organique*, the *Handwörterbuch der Chemie*, &c.). Griess, on the contrary, in a recent memoir (Phil. Trans. 1864, [4] 708) designates the base obtained from the nitrated phenylamides as α, and that obtained by reduction of dinitrobenzene as β-nitraniline.

2. Of *β-nitraniline*.—Nitro-phenyl-pyrotartrimide is dissolved in a boiling dilute solution of sodic carbonate mixed with a little caustic soda, whereby it is converted, by taking up 1 at. water, into nitrophenyl-pyrotartramic acid, and the solution is boiled till it no longer gives a precipitate of that acid on addition of nitric acid. The nitrophenyl-pyrotartramic acid is then resolved into β-nitraniline and pyrotartaric acid. The yellow solution yields on cooling an abundant crop of yellow rhombic tables which must be collected on a filter, washed with cold water, and purified by recrystallisation. (Arppe.)

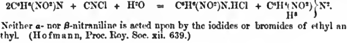
An easier mode of preparation is to dissolve phenylacetamide or phenylsuccinamide in cold fuming nitric acid, dilute the solution with water, which throws down nitrophenyl-acetamide or nitrophenyl-succinamide, and distil this precipitate with caustic potash. (Hofmann.)

*Properties*.—Alpha-nitraniline forms needles of a fine yellow colour and an inch long; heavier than water. They melt at about 110° (at 108°, according to Arppe), forming an oil of a deep yellow colour, which boils at 285°, passes over in yellow vapours, and solidifies in the receiver, forming a laminated mass; at 100° the crystals sublime in beautiful laminæ, without previous fusion (Hofmann and Muspratt). The sublimed crystals are rhombic tables of 51° and 129°, having one of the acute angles either perpendicularly truncated, or bevelled with two faces, while the two obtuse angles are sometimes obliquely truncated, sometimes unaltered; macles are often formed with deep re-entering angles. Similar modifications are exhibited by the crystals obtained from solution in water or alcohol (Arppe). The crystals are inodorous at ordinary temperatures, but when slightly warmed, they emit an aromatic odour having a distant resemblance to that of aniline; they have a burning sweet taste, are perfectly neutral, and colour firwood (as well as the cuticle) deep yellow, like aniline, but do not produce any blue colour with chloride of lime. (Hofmann and Muspratt.)

β-nitraniline crystallises from the aqueous solution by slow cooling in long needles; but by more rapid cooling, in small tabular or needle-shaped crystals with angles of 69° and 111°, having the smaller angle truncated in such a manner as to produce a six-sided table with angles of 111° and 138°. From an alcoholic solution, the rhombic tables separate unaltered together with the six-sided tables; an ethereal solution yields sometimes tables, sometimes capillary needles; from an aqueous solution containing carbonate of sodium, rhombic tables of 55° and 125° are obtained; by sublimation, sometimes needles, sometimes irregular laminæ. The crystals melt at 141°, volatilise at about the same temperature, and sublime very beautifully when heated between two watch-glasses. At 100°, the sublimation is scarcely perceptible. The crystals have also scarcely any taste. (Arppe.)

Alpha-nitraniline dissolves in 600 pts. of *water* at 18·5°, and much more readily in boiling water (Arppe). β-nitraniline dissolves in 1250 pts. of water at 12·5°, and in 45 pts. of boiling water. Both modifications dissolve easily in *alcohol* and in *ether*.

*Decompositions*.—1. The vapour of nitraniline burns with a bright sooty flame.—2. Alpha-nitraniline distils almost without residue; but β-nitraniline leaves a considerable quantity of carbonaceous matter, when distilled.—3. *Bromine* converts nitraniline, with great rise of temperature and evolution of hydrobromic acid, into a brown resin whose solution in hot alcohol deposits yellow crystals, insoluble in water, acids, and alkalis, and probably consisting of dibromonitraniline, $C^6H^4Br^2(NO^2)N$ (Hofmann and Muspratt).—4. *Nitric acid*, even when highly concentrated, dissolves β-nitraniline without visible decomposition (Arppe); but α-nitraniline is violently acted upon by nitric acid, and converted, after a while, into an acid which appears to be picric acid (Hofmann and Muspratt).—Gaseous *chloride of cyanogen* passed through melted nitraniline (α), converts part of it into dinitromelaniline, while the greater portion is transformed into a resinous substance. Alcoholic nitraniline is decomposed very slowly by chloride of cyanogen and aqueous aniline in a peculiar manner; but nitraniline dissolved in ether forms with chloride of cyanogen, nothing but hydrochlorate of aniline and yellowish needles of nitrophenyl-carbamide:



$$2C^6H^6(NO^2)N + CNCl + H^2O = C^6H^6(NO^2)N.HCl + \left.\begin{matrix}(CO)''\\C^6H^4(NO^2)\\H^3\end{matrix}\right\}N^2.$$

6. Neither α- nor β-nitraniline is acted upon by the iodides or bromides of ethyl and methyl. (Hofmann, Proc. Roy. Soc. xii. 639.)

Salts of Nitraniline.—Nitraniline in either modification is a very weak base, not precipitating any metallic salt. From the solutions of its salts, some of which are crystallisable; it is precipitated in the crystalline form by aniline, as well as by the caustic alkalis and alkaline carbonates.

*Hydrochlorates.* $C^6H^6N^2O^2.HCl$.—The colourless solution of α-nitraniline in hydrochloric acid, yields by evaporation, nacreous crystals, extremely soluble in water and alcohol (Hofmann and Muspratt). Elongated rhombic tables with angles of 120° and 60°, which are permanent in the air and dissolve readily in hydrochloric acid; they are decomposed by water, which separates the greater part of the base. (Arppe.)

β-nitraniline forms with hydrochloric acid, a yellow solution, or if the acid is in great excess, a colourless solution, which, on cooling, deposits rather large, colourless, tabular crystals, which in their simplest form, are four-sided tables, with angles either (*a*) of 95° and 85°, or (*b*) of 65° and 115°; by the combination of these two forms, the acute angles of *a* being truncated by *b*, six-sided tables are formed; and by the truncation of all the angles of *a*, eight-sided tables. The salt is easily decomposed, both by heat, which causes it to turn yellow and give off acid, and by water, which separates, the base almost completely; alkalis precipitate the nitraniline in the crystalline form but the precipitate redissolves in excess of the alkali. (Arppe.)

*Chloroplatinates*, $2[C^6H^6(NO^2)N.HCl].Pt^{iv}Cl^4$.—The α-salt is precipitated by platinic chloride from the alcoholic, but not from the aqueous solution of α-nitraline, as a yellow crystalline powder, which is extremely soluble in water and in alcohol, and must therefore be washed with ether. The β-salt is precipitated from the concentrated solution of the hydrochlorate either in water or in alcohol; it is, however, much more soluble in alcohol than in water. It crystallises in stellate groups of very slender needles. When washed with a mixture of alcohol and ether, it is converted into a yellow salt, apparently consisting of $C^6H^6(NO^2)N.HCl.Pt^{iv}Cl^4$. (Arppe.)

*Nitrate of α-nitraniline* is crystalline, easily soluble in water, very sparingly soluble in strong nitric acid. The *β-nitrate* crystallises in shining, long, right-angled truncated prisms, and is decomposed by water.

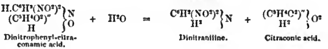
*Oxalates.*—Alpha-nitraniline forms an acid oxalate, $C^6H^6(NO^2)N.C^2H^2O^4$, which is deposited in yellow crystals on mixing the alcoholic solutions of the base and acid. Oxalate of β-nitraniline crystallises in slender needles and plates sparingly soluble in water.

*Sulphates.*—The α-salt crystallises in shining rhombic prisms, which dissolve in water, forming a clear solution. The β-salt crystallises from a solution of β-nitraniline in dilute sulphuric acid, in large shining plates which have an acid taste, and are decomposed by water.

*Tartrate of α-nitraniline* forms a yellow solution from which the salt crystallises in yellow rectangular tables. Potash decomposes the solution, separating the base in the form of a yellow crystalline precipitate soluble in excess of the alkali. *Tartrate of β-nitraniline* crystallises in yellow needles; potash does not precipitate, but dissolves it, forming a red solution. (Arppe.)

A solution of either modification of nitraniline, mixed with a recently prepared solution of *gall-nuts*, and afterwards with a small quantity of potash, yields a copious flocculent or almost gummy precipitate, which is decomposed by excess of potash, a portion of the base being precipitated in the crystalline form. (Arppe.)

**Dinitraniline.** $C^6H^5N^3O^4 = \left.\begin{array}{c}C^6H^3(NO^2)^2\\H^2\end{array}\right\}N$. (Gottlieb, Ann. Ch. Pharm. lxxxv. 17.)—Produced by the action of alkalis on dinitrophenyl-citraconimide. When this compound is treated with a boiling dilute solution of carbonate of sodium, carbonic anhydride is evolved, and the light flocculent crystals of the amide are partly dissolved, and partly converted into a heavy yellow, crystalline powder, consisting of dinitraniline; when the action is complete, this substance separates out in more definite crystals. If the boiling be not continued long enough to ensure the complete decomposition of the imide in the manner above-mentioned, the mother-liquor is found to contain dinitrophenylcitraconamate of sodium as well as citraconate. The dinitraniline is purified by crystallising it several times from boiling water:



$$\left.\begin{array}{c}(C^5H^4O^2)''\\C^6H^3(NO^2)^2\end{array}\right\}N + H^2O = \left.\begin{array}{c}H.C^6H^3(NO^2)^2\\(C^5H^4O^2)''\\H\end{array}\right\}\begin{array}{c}N\\O\end{array}$$

Dinitrophenyl-citraconimide. Dinitrophenyl-citraconamic acid.

$$\left.\begin{array}{c}H.C^6H^3(NO^2)^2\\(C^5H^4O^2)''\\H\end{array}\right\}\begin{array}{c}N\\O\end{array} + H^2O = \left.\begin{array}{c}C^6H^3(NO^2)^2\\H^2\end{array}\right\}N + \left.\begin{array}{c}(C^5H^4C^2)''\\H^2\end{array}\right\}O^2$$

Dinitrophenyl-citraconamic acid. Dinitraniline. Citraconic acid.

Dinitraniline crystallises by spontaneous evaporation of its solution in a mixture of alcohol and ether, in greenish-yellow, rather brilliant tables, exhibiting a bluish tint by reflected light on the lateral faces. It is inodorous; boils at 185°, giving off yellow vapours, which condense in the form of a yellow sublimate; the melted portion solidifies on cooling into a deep yellow crystalline mass. It dissolves sparingly in cold *water*, easily in boiling water and in *alcohol*. When heated suddenly in a tube, it blackens and explodes. *Sulphide of ammonium* converts it into nitrophenylene-diamine:

$$\underset{\text{Dinitraniline.}}{\left.\begin{matrix}C^6H^3(NO^2)^2\\H^2\end{matrix}\right\}N} + 3H^2S = \underset{\text{Nitrophenylene-diamine.}}{\left.\begin{matrix}[C^6H^3(NO^2)]''\\H^4\end{matrix}\right\}N^2} + 2H^2O + S^3.$$

Dinitraniline does not combine with acids.

**Trinitraniline.** *Trinitrophenylamide, Picramide*, $C^6H^4N^4O^6 = \left.\begin{matrix}C^6H^2(NO^2)^3\\H^2\end{matrix}\right\}N$ ? (Pisani, Ann. Ch. Pharm. xcii. 326.)—Obtained by the action of ammonia on chloride of trinitrophenyl or chloropicryl (p. 416). When crude chloropicryl is triturated with excess of cold aqueous carbonate of ammonium, and the resulting mass is treated with boiling water, a residue is obtained, consisting of trinitraniline, which dissolves in boiling alcohol, and separates in crystalline plates, dark yellow by transmitted, violet by reflected light, and yielding a light yellow powder. It dissolves sparingly in ether. When heated it decomposes with detonation, giving off nitrous fumes and leaving a carbonaceous residue. Heated with aqueous potash, it gives off ammonia and leaves picrate of potassium.

**Azonitrophenylamine,** $C^6H^3N^3O^2 = C^6H^3(NO^2)N^2 = \left.\begin{matrix}[C^6H(NO^2)N''']'\\H^2\end{matrix}\right\}N.$ *Diazonitrobenzol.* (Griess, Phil. Trans. 1864, [3], 708.)—By treating the nitrates of α- and β-nitraniline* with nitrous acid, nitrates of azonitrophenylamine are obtained, having the same composition but differing from one another in physical properties, and yielding, when heated with bromine, platinic chloride, and other reagents, isomeric salts exhibiting corresponding differences of physical character.

*Nitrate of α-azonitrophenylamine*, $C^6H^3N^3O^2.NHO^3$, is precipitated by ether from its alcoholic solution in prisms frequently approaching to cubes, very soluble in water, sparingly soluble in alcohol, insoluble in ether, and exploding with great violence when heated. The β-salt has about the same degree of solubility, but crystallises in fine long needles.

Both modifications of the nitrate when boiled with water, are decomposed, after some time, with evolution of nitrogen-gas, yielding a brownish, easily fusible, slightly acid substance, which, judging from the manner in which the nitrates of azophenylamine azobromo-bromophenylamine, &c., are decomposed (pp. 432, 437), should have the composition of nitrophenic acid, according to the equation:

$$\underset{\text{Azonitrophenylamine.}}{C^6H^3(NO^2)N^2} + H^2O = \underset{\text{Nitrophenic acid.}}{C^6H^5(NO^2)O} + N^2;$$

but it cannot be made to crystallise, and appears to differ altogether in its properties, both from nitrophenic and from isonitrophenic acid (p. 394).

The *chloroplatinates*, $2(C^6H^3N^3O^2.HCl)Pt^{iv}Cl^4$, of both modifications, crystallises in long yellow needles or prisms.

*Perbromide of α-azonitrophenylammonium*, $C^6H^4(NO^2)N^2Br^3$, is precipitated by bromine-water from the aqueous solution of the α-nitrate, usually as an oil which soon solidifies. It forms small orange-coloured plates or prisms, which, unlike the β-compound, cannot be recrystallised from warm alcohol. It is likewise obtained, together with tribromonitraniline, by the action of bromine on azodinitrodiphenyldiamine, the latter being suspended in water, and bromine added till the whole is converted into a heavy brownish-red oil:

$$\underset{\text{Azodinitro-diphenyl-diamine.}}{C^{12}H^8(NO^2)^2N^4} + Br^8 = \underset{\text{Perbromide.}}{C^6H^4(NO^2)N^2Br^3} + \underset{\text{Tribromonitraniline.}}{C^6H^3Br^3(NO^2)N} + 2HBr.$$

On decanting the supernatant aqueous mother-liquor, and allowing the excess of bromine to evaporate, the oil solidifies to a crystalline mass. Before however complete solidification occurs, thick yellowish-red crystals frequently shoot out, consisting of the nearly pure perbromide, which may be freed from adhering tribromaniline by pulverisation and washing with ether. If no distinct crystals form after the bromine has evaporated, the crystalline mass, consisting of the perbromide and tribromonitraniline, must be pressed between filter-paper and washed with ether, to dissolve out the tribromonitraniline. This however is attended with loss, since the perbromide is partly converted by the ether into nitrobromobenzene.

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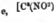
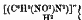
* The prefixes α and β are here used in the sense opposite to that assigned to them in Griess's paper (see foot-note, p. 445).

The β-perbromide is precipitated by bromine-water from the aqueous β-nitrate, in slender orange prisms almost insoluble in water and in ether, but easily soluble in warm alcohol, whence the compound is deposited on cooling in well-defined crystals.

On heating the alcoholic solutions of the α- and β-perbromide, α- and β-nitrobromobenzene, $C^6H^4(NO^2)Br$ (p. 416), are obtained.

The α-perbromide treated with aqueous ammonia is converted into α-azo-nitrophenylene-diamine,  $\left.\begin{matrix}[C^6(NO^2)N''']'' \\ H^4\end{matrix}\right\}N^3$, or diazonitrobenzolimide,  $\left.\begin{matrix}[(C^6H^3(NO^2)N^2)]'' \\ H^2\end{matrix}\right\}N$, which crystallises in orange-coloured needles, melting at 52°. The β-perbromide yields in like manner a compound having the same composition, but crystallising in very brilliant yellow rounded plates which melt at 71°.

**Tribromonitrophenylamine,** or **Tribromonitraniline,** $C^6H^3Br^3(NO^2)N$.—Produced as above by the action of bromine on azodinitrodiphenyldiamine. To obtain it pure, the ethereal solution is evaporated to dryness; the residue is dissolved in warm alcohol; the solution is mixed with water till it becomes milky and deposits crystals, and the crystals are thrown on a filter, pressed between sheets of filter-paper to remove any adhering nitrobromobenzene, and further purified by crystallisation from weak alcohol. It crystallises in small slightly yellowish plates which cannot be sublimed without decomposition. (Griess.)

## II. Derivatives of Aniline formed by replacement of Hydrogen not belonging to the Phenyl-radicle.

The extra-radical or typic hydrogen of aniline may be replaced wholly or partially, both by acid and by alcohol-radicles. In the former case, neutral or acid amides are produced, such as phenyl-acetamide,* $(C^6H^5)(C^2H^3O)HN$, phenyl-dibenzoylamide, $(C^6H^5)(C^7H^5O)^2N$, &c. These compounds are described with the several acids, or in separate articles. In the latter case, basic amines are formed, such as methyl-aniline, $(C^6H^5)(CH^3)HN$, methyl-amylaniline, $C^6H^5)(CH^3)(C^5H^{11})N$, &c.: these will be described in the following pages. They are produced by the action of the bromides and iodides of the alcohol-radicles on aniline: those in which the whole of the hydrogen is replaced by alcohol-radicles are capable of uniting with the alcoholic iodides, forming compounds belonging to the ammonium-type (see Phenylammoniums).

**Allylaniline,** or **Allylophenylamine,** $C^9H^{11}N$ = $\left.\begin{matrix}C^6H^5 \\ C^3H^5 \\ H\end{matrix}\right\}N$. (H. Schiff, Ann. Ch. Pharm. Suppl. iii. 364.)—A mixture of aniline and iodide of allyl becomes heated to 100° in a few minutes, and forms a very soluble crystalline mass of hydriodate of allylaniline. The free base separated from this salt by potash is a yellow liquid of specific gravity 0·982 at 25°; having an odour of aniline and of geraniums, and a burning taste; slightly soluble in water. Its salts are crystalline, easily soluble, and are coloured violet by hypochlorite of calcium. The concentrated solution of the hydrochlorate gives with *platinic chloride* a dark yellow precipitate, which usually separates as a resin becoming crystalline after a while. It is slightly soluble in water and in alcohol, and contains $2(C^9H^{11}N.HCl)Pt^{iv}Cl^4$ (p. 459).

The free base treated with *œnanthol* yields heptylidene-diallyl-diphenyl-diamine, $(C^7H^{14})''(C^3H^5)^2(C^6H^5)^2N^2$.

**Amylaniline,** $C^{11}H^{17}N$ = $\left.\begin{matrix}C^6H^5 \\ C^5H^{11} \\ H\end{matrix}\right\}N$. (Hofmann, Chem. Soc. Qu. J. iii. 297; Ann. Ch. Pharm. lxxiv. 153.)—To obtain this base, a mixture of aniline and bromide of amyl is set aside at the ordinary temperature for several days; the mother-liquor, consisting of amylaniline and bromide of amyl, is decanted from the resulting crystals of hydrobromate of aniline; and the bromide of amyl is distilled off:

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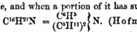
* *Note to Phenylacetamide* (p. 418). This compound is easily produced by prolonged boiling (cohobation) of aniline with concentrated acetic acid ($C^6H^7N + C^2H^4O^2 - H^2O = C^8H^9NO$). On subsequent distillation, the amide passes over and solidifies in a white paraffin-like mass. It dissolves easily in water, alcohol, ether, benzene, and volatile oils; crystallises on cooling from a hot aqueous solution in small colourless needles; from oil of lemons, in large needles. It melts at 101°, and boils at 295° (bar. at 755 mm.). Specific gravity = 1·0 9 at 10·5°. Vapour-density, obs. = 4·807—4·887; calc. = 4·671. It is decomposed by sodium, yielding aniline and a small quantity of another basic oil (Greville Williams, Chem. Soc. J. xvii. 106.)

$$\mathrm{2C^6H^7N + C^5H^{11}Br = C^6H^7N.HBr + C^{11}H^{17}N.}$$

Or a mixture containing a larger quantity of bromide of amyl is heated in the water-bath; the excess of bromide of amyl removed by distillation; and the remaining hydrobromate of amylaniline decomposed by potash, whereby the amylaniline is separated in the form of an oil, which may be purified by solution in ether, agitation with water, and evaporation of the ether.

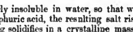
Amylaniline is a colourless oil, which boils steadily at 258°, has an agreeable odour like that of roses at ordinary temperatures, but an offensive odour of fusel-oil when heated. Heated with bromide of ethyl to 100°, it is converted into hydrobromate of ethylamylaniline, and with bromide of amyl into diamylaniline.

Its compounds with hydrobromic, hydrochloric and oxalic acids, form beautiful crystals, which have a fatty lustre, dissolve sparingly in water, and when heated with water, rise to the surface in the form of an oil which solidifies on cooling.—The chloroplatinate is precipitated in the form of an unctuous mass, which crystallises only after a considerable time, and when a portion of it has suffered decomposition.


**DIAMYLANILINE**, $\mathrm{C^{16}H^{27}N} = \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{(C^5H^{11})^2}\end{matrix}\right\}\mathrm{N}$. (Hofmann, Ann. Ch. Pharm. lxxiv. 156.)

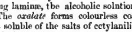
Amylaniline heated for two days in the water-bath with excess of bromide of amyl, yields crystals of hydrobromate of diamylaniline, from which the base may be separated as above. It is an oil boiling between 275° and 280°, and having the odour of amylaniline.

Its salts are nearly insoluble in water, so that when the base is heated with dilute hydrochloric or sulphuric acid, the resulting salt rises to the surface in the form of an oil, which on cooling solidifies in a crystalline mass having a fatty lustre.—The *platinum-salt*, $\mathrm{2(C^{16}H^{27}N.HCl)Pt^{iv}Cl^4}$, is precipitated, on mixing the hydrochlorate with tetrachloride of platinum, in the form of a yellow oil which quickly solidifies to a brick-red crystalline mass; alcoholic solutions immediately yield crystals.


**Cetylaniline,** $\mathrm{C^{12}H^{39}N} = \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{C^{16}H^{33}}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$. (Fridan, Ann. Ch. Pharm. lxxxiii. 25.)—Iodide of cetyl heated to 100° with excess of aniline yields crystalline hydriodate of aniline and free cetylamine, which may be separated from the crystals by means of water and ether, and purified by converting it into a hydrochlorate, decomposing this salt by potash, and recrystallising the free base thus obtained from alcohol.

Cetylaniline crystallises in silvery scales which melt at 42°, and solidify at 32° to a yellowish-white mass of crystalline rosettes. It is insoluble in *water*, easily soluble in *alcohol* and *ether*, does not precipitate metallic salts, and has no action on vegetable colours.

The *hydrochlorate* crystallises in shining plates.—The *chloroplatinate* $\mathrm{(2C^{22}H^{39}N.HCl).Pt^{iv}Cl^4}$, is precipitated in reddish-yellow crystalline flocks on adding water to a mixture of hydrochlorate of cetylaniline and alcoholic platinic chloride. The *nitrate* crystallises in shining laminæ, the alcoholic solution of which is partially decomposed by evaporation. The *oxalate* forms colourless confusedly interlaced needles. The *sulphate* is the most soluble of the salts of cetylaniline; it may be completely separated from its alcoholic solution by water.


**Ethylaniline.** $\mathrm{C^8H^{11}N} = \left.\begin{matrix}\mathrm{C^6H^5}\\ \mathrm{C^2H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$. (Hofmann, Chem. Soc. Qu. J. iii. 285; —Ann. Ch. Pharm. lxxiv. 128.)—A mixture of aniline and excess of bromide of ethyl, gently heated in an apparatus which allows the condensed vapours to flow back again, passes into spontaneous ebullition, and afterwards on cooling yields crystals of hydrobromate of ethylaniline: $\mathrm{C^6H^7N + C^2H^5Br = C^8H^{11}N.HBr}$. The aqueous solution of the hydrobromate of ethylaniline is mixed with concentrated potash, and the brown oil which rises to the surface is removed with the pipette, dried over hydrate of potassium, and rectified.

Ethylaniline is a transparent, colourless, strongly refracting oil of sp. gr. 0·954 at 18°; boils constantly at 204°; smells like aniline; does not produce any blue colour with chloride of lime; colours firwood and elder-pith yellow, but much less strongly than aniline. It is soluble in alcohol.

*Decompositions.*—1. Ethylaniline quickly turns brown when exposed to the air, or even under the mere influence of light.—2. With *bromine* it forms a neutral (tribromaniline?) and a basic compound.—3. It takes fire in contact with dry *chromic acid*.—4. With *phosgene gas* it acts violently, forming a hydrochlorate and an indifferent oil.—

5. With *sulphide of carbon*, it slowly gives off sulphuretted hydrogen.—6. *Cyanogen gas* passed through alcoholic ethylaniline, forms short prisms probably consisting of cyanethylaniline, $C^9H^{11}N^2$. This compound is separated in the pulverulent form, on adding ammonia to the solution of the crystals in dilute sulphuric acid: its solution in sulphuric acid, on being mixed with strong hydrochloric acid, deposits the hydrochlorate in beautiful crystals; its platinum-salt is very soluble.—7. Ethylaniline absorbs gaseous *chloride of cyanogen* rapidly and with rise of temperature, and then solidifies on cooling in the form of a resinous mixture containing a neutral oil and the hydrochlorate of a volatile oily base.—8. Ethylaniline heated for two days in the water-bath with *iodide of methyl* yields crystals of hydriodate of methyl-ethyl-aniline $(C^6H^5)(CH^3)(C^2H^5)N.HI$. In like manner with *bromide of ethyl* and *bromide of amyl*, it yields the hydrobromates of diethylaniline $(C^6H^5)(C^2H^5)^2N$, and ethyl-amyl-aniline $(C^6H^5)(C^2H^5)(C^5H^{11})N$.

*Combinations.*—The salts of ethylaniline dissolve very easily in water, less easily in alcohol, from which also they crystallise better. The sulphate and hydrochlorate have not yet been obtained in the solid form. The *hydrobromate*, $C^8H^{11}N.HBr$, prepared as above, crystallises from the alcoholic solution by spontaneous evaporation in large tables. At a gentle heat it sublimes in needles without decomposition, but when quickly heated, it is resolved into aniline and bromide of ethyl. It dissolves very readily in water.

*Mercuric chloride* and *trichloride of gold* added to hydrochlorate of ethylaniline throw down yellow oils which quickly decompose.

*Chloroplatinate of Ethylaniline*, $2(C^8H^{11}N.HCl).Pt^{iv}Cl^4$.—A saturated aqueous solution of hydrochlorate of ethylaniline, added to a concentrated solution of platinic chloride, throws down an oil of a deep orange-yellow colour, which, after a few hours, solidifies in the crystalline form; a somewhat more dilute mixture deposits after a few hours, splendid needles an inch long, which must be washed with a mixture of ether and a little alcohol. The crystals are permanent at 100°, and dissolve very readily in water and alcohol.

**DIETHYLANILINE.** $C^{10}H^{15}N = \left.\begin{matrix} C^6H^5 \\ (C^2H^5)^2 \end{matrix}\right\} N.$ (Hofmann, Ann. Ch. Pharm. lxxiv. 135.)—The hydrobromate of this base separates in crystals from a mixture of ethylaniline with a very large excess of bromide of ethyl, and when freed from adhering bromide of ethyl, and treated with potash, as in the preparation of ethylaniline, yields diethylaniline, as a transparent, colourless oil of sp. gr. 0·936 at 18°, boiling with perfect steadiness at 213·5°, and exhibiting with firwood and chloride of lime, the same reactions as ethylaniline. It remains transparent and colourless when exposed to the air. With *iodide of ethyl* it yields iodide of triethyl-phenylammonium, $(C^2H^5)^3(C^6H^5)NI$.

*Hydrobromate of Diethylaniline*, $C^{10}H^{15}NHBr$, prepared as above, forms large four-sided tables, which at a gentle heat melt and sublime in needles without decomposition; but when quickly heated, are almost wholly resolved into an oily distillate consisting of ethylaniline and bromide of ethyl.

*Chloroplatinate of Diethylaniline*, $2(C^{10}H^{15}N.HCl).Pt^{iv}Cl^4$, is precipitated from somewhat concentrated solutions of hydrochlorate of diethylaniline and tetrachloride of platinum, in the form of a brownish-yellow oil which soon solidifies in a hard mass; but from more dilute solutions it is gradually deposited in yellow prisms which may be purified by crystallisation from alcohol. It is less soluble both in alcohol and in water than the platinum-salt of ethylaniline. (Hofmann.)

**ETHYLBROMANILINE.** $C^8H^{10}BrN = \left.\begin{matrix} C^6H^4Br \\ C^2H^5 \\ H \end{matrix}\right\} N.$ Bromaniline treated with excess of bromide of ethyl is quickly converted into hydrobromate of ethylbromaniline (p. 278) which, when treated with potash, yields ethylbromaniline exactly resembling ethylchloraniline. Its platinum-salt is a viscid oil. (Hofmann, Ann. Ch. Pharm. lxxiv. 125.)

**ETHYLCHLORANILINE.** $C^8H^{10}ClN = \left.\begin{matrix} C^6H^4Cl \\ C^2H^5 \\ H \end{matrix}\right\} N.$—A mixture of chloraniline and excess of bromide of ethyl, kept for some days at 100°, and then freed from excess of bromide of ethyl by distillation with water, leaves a solution of hydrobromate of ethylchloraniline, on which a few drops of the base float. This base is completely separated by potash in the form of an oil of high boiling point, remaining liquid below 0°, and having an odour like that of anise-oil.

The salts of this base are much more soluble than those of chloraniline.

The *sulphate* and *oxalate* crystallise; the *chloroplatinate* does not. (Hofmann, Ann. Ch. Pharm. lxxiv. 143.)

Diethylchloraniline. $C^{10}H^{14}ClN = \left.\begin{matrix}C^6H^4Cl\\(C^2H^5)^2\end{matrix}\right\}N$.—A mixture of bromide of ethyl and ethylchloraniline dried in a hot current of air and heated to 100° for two days, is converted into hydrobromate of diethylchloraniline; and from this the base is separated by potash as a brownish oil, which is purified by solution in ether, freed from potash by washing with water, and from ether by evaporation.

The solution of the base in hydrochloric acid yields with *platinic chloride* an orange-yellow crystalline precipitate of the chloroplatinate $2(C^{10}H^{14}ClN.HCl).Pt^{iv}Cl^4$. (Hofmann, *loc. cit.*)

Ethyl-allyl-aniline. $C^{11}H^{15}N = \left.\begin{matrix}C^6H^5\\C^2H^5\\C^3H^5\end{matrix}\right\}N$.—The hydriodate is obtained by heating allylaniline with iodide of ethyl for two or three days, as a crystalline mass, from which potash separates the base as a thick yellow oil having no characteristic odour, distilling between 220° and 225°, and forming soluble salts. An *acid oxalate*, $C^{11}H^{15}N.C^2H^2O^4$, crystallises from a solution of the base in excess of hot aqueous oxalic acid, in spherical groups of small needles. (Schiff, Ann. Ch. Pharm. Suppl. iii. 364.)

Ethyl-amyl-aniline. $C^{13}H^{21}N = \left.\begin{matrix}C^6H^5\\C^2H^5\\C^5H^{11}\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. lxxiv. 156).—A mixture of amylaniline and excess of bromide of ethyl (*vid. sup.*), or of ethylaniline and excess of bromide of amyl or of iodide of amyl, which acts most quickly, is heated in the water-bath for two days, and the base is separated from the resulting hydrobromate of ethylamylaniline as in the preceding case. The product is a colourless oil, boiling at 262°, therefore only 4° higher than amylaniline.

When heated with *iodide of methyl* it yields the iodide of methyl-ethyl-amylo-phenylammonium, $(CH^3)(C^2H^5)(C^5H^{11})(C^6H^5)NI$.

The *Hydrobromate* and *Hydrochlorate of Ethylamylaniline* crystallise. The former is resolved by distillation into ethylaniline and bromide of amyl:

$$C^{13}H^{21}N.HBr \quad = \quad C^8H^{11}N \ + \ C^5H^{11}Br.$$

The *chloroplatinate* is precipitated in the form of an orange-yellow viscid liquid, which solidifies in crystals fusible at 100°

**Methylaniline.** $C^7H^9N = \left.\begin{matrix}C^6H^5\\CH^3\\H\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. lxxiv. 150.) —This base, metameric with benzylamine or toluidine, $(C^7H^7)H^2N$, is produced by the action of iodide or bromide of methyl on aniline. The mixture, which should be made gradually, to avoid too great a rise of temperature, soon solidifies to a crystalline mass of hydriodate or hydrobromate of methylaniline, from the aqueous solution of which the oily base may be separated by potash.

Methylaniline is a transparent oil, which boils at 192°, has a peculiar odour, and colours aqueous chloride of lime violet, but not so strongly as aniline. Its salts are sparingly soluble in water, and are separated from their aqueous solution in the crystalline state by acids.

The *chloroplatinate*, $2(C^7H^9N.HCl).Pt^{iv}Cl^4$, is precipitated in the form of a limpid oil, quickly changing to pale yellow crystalline scales which must be quickly washed with cold water and dried. They soon turn black from decomposition, and when alcoholic solutions are used, a black mass is immediately precipitated.

The *oxalate* crystallises readily, but quickly decomposes, reproducing aniline.

Methyl-amyl-aniline, $C^{12}H^{19}N = \left.\begin{matrix}C^6H^5\\CH^3\\C^5H^{11}\end{matrix}\right\}N$, is produced by the distillation of hydrate of methyl-ethyl-amylo-phenylammonium, water and ethylene being given off at the same time:

$$[(CH^3)(C^2H^5)(C^5H^{11})(C^6H^5)N]HO \quad = \quad (CH^3)(C^5H^{11})(C^6H^5)N \ + \ C^2H^4 \ + \ H^2O.$$

It is an oil having an agreeable odour. The *chloroplatinate*, $2(C^{12}H^{19}N.HCl).Pt^{iv}Cl^4$, is a crystalline precipitate. (Hofmann, Ann. Ch. Pharm. lxxix. 15.)

Methyl-ethyl-aniline. $C^9H^{13}N = \left.\begin{matrix}C^6H^5\\CH^3\\C^2H^5\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. lxxiv. 152.)—Ethylaniline heated with iodide of methyl for two days to 100°, yields crystals of hydriodate of-methyl-ethyl-aniline. The base separated therefrom smells like ethylaniline, but is not coloured by chloride of lime. Its salts are very soluble and mostly uncrystallisable.

**Phenylanilines.**—1. DIPHENYLAMINE, $C^{12}H^{11}N = \left.\begin{matrix}C^6H^5\\C^6H^5\\H\end{matrix}\right\}N$. (Hofmann, Ann. Ch. Pharm. cxxxii. 163.)—This base, isomeric with xenylamine $(C^{12}H^9)H^2N$, is produced by the distillation of triphenyl-rosaniline (aniline-blue), $C^{20}H^{16}(C^6H^5)^3N^3$. When commercial aniline-blue is subjected to distillation, a faintly yellowish liquid passes over, and when the portion which distils between 280°—300° is mixed with hydrochloric acid, it immediately solidifies to a hydrochlorate, sparingly soluble in strong hydrochloric acid, easily purified by washing with alcohol and recrystallisation from alcohol. This salt mixed with ammonia yields colourless oil-drops which solidify in a few seconds to a hard crystalline mass of diphenylamine.

This base is also found in small quantity amongst the products of distillation of rosaniline, leucaniline, and melaniline.

Diphenylamine has a peculiar odour of flowers, and an aromatic taste with burning after-taste. It melts at 45° to a yellow oil, which boils constantly at 310°. It is nearly insoluble in *water*, easily soluble in *alcohol* and *ether*. Neither the aqueous nor the alcoholic solution exhibits the slightest alkaline reaction. The crystals treated with concentrated acids are immediately converted into the corresponding salts, which however are extremely unstable, the base being separated from them even by water in oily drops which soon solidify to crystals. From the hydrochlorate every trace of the base may be removed by prolonged washing with water. The *hydrochlorate*, $C^{12}H^{11}N.HCl$, is obtained by recrystallisation from alcohol in white needles, which soon turn blue in contact with the air.

Diphenylamine and its salts treated with strong *nitric acid* immediately assume a splendid blue colour; the reaction is best exhibited by mixing the base with hydrochloric acid, and then adding nitric acid by drops; it is very delicate, and serves to distinguish diphenylamine from all similar bodies excepting phenyl-tolylamine (p. 454). The compound to which this blue colour is due is likewise produced by the action of other oxidising agents; thus on mixing a solution of the hydrochlorate with *platinic chloride*, a blue solution is formed, from which the chloroplatinate separates only on very strong concentration, and even then deeply coloured.

When diphenylamine is mixed with *toluidine* (benzylamine) and the mixture treated with *mercuric chloride* or *arsenic acid*, or any of the other reagents by which ordinary aniline is converted into aniline-red, a fused mass is obtained which dissolves in alcohol with splendid violet-blue colour. The body thus formed, which has the character of a true dye-stuff, is probably monophenyl-rosaniline, $C^{20}H^{18}(C^6H^5)N^3.H^2O$.

An alcoholic solution of diphenylamine mixed with *bromine*, yields a yellow crystalline precipitate of tetrabromo-diphenylamine, $C^{12}H^7Br^4N$, probably $= (C^6H^3Br^2)^2HN$. It is sparingly soluble in cold alcohol, and separates from boiling alcohol in beautiful silky crystals.

Diphenylamine heated with *chloride of benzoyl* yields diphenyl-benzamide, $\left.\begin{matrix}(C^6H^5)^2\\C^7H^5O\end{matrix}\right\}N$, in the form of a thick oil which crystallises on cooling. (See PHENYL-BENZAMIDES).

2. TRIPHENYLAMINE. $C^{18}H^{15}N = (C^6H^5)^3N$. *Diphenyl-aniline.* (Göessmann, Ann. Ch. Pharm. c. 57.)—This base has not yet been obtained directly from aniline or any other phenyl-compound; but a base metameric, or possibly identical, with it is produced by the distillation of sulphate of cinnamyl and ammonium with slaked lime:

$$2[C^9H^7(NH^4)SO^4] + Ca''H^2O^2 = C^{18}H^{15}N + NH^3 + 2H^2O + Ca''H^2S^2O^8.$$

The distillate, which consists of a dark yellow oily liquid and a watery ammoniacal liquid containing the organic base, is boiled with carbonate of sodium or dilute potash-ley, till all the ammonia and volatile hydrocarbon, &c., are expelled; the fixed alkali removed by repeated washing, &c., with diminishing quantities of hot water; and, after the water has been separated as completely as possible by decantation, the oily base is distilled in a slow stream of hydrogen, the temperature being kept low at first to evaporate the water, and the base afterwards distilled off between 140° and 150°; this temperature should be kept up as long as possible, since the base decomposes at higher temperatures.

The base thus obtained is a colourless oily liquid, which, on exposure to the air, becomes yellow at first, and afterwards red. It boils between 140° and 150°, and dissolves sparingly in *water*, readily in *alcohol* and *ether*.

The salts are very unstable, all of them, excepting the chloroplatinate, decomposing spontaneously on exposure to the air either in aqueous or alcoholic solution. The *hydrochlorate* crystallises in shining laminæ having a slight tinge of red. The *chloro-*

*platinate*, $2C^{18}H^{16}NCl.Pt^{iv}Cl^4$, separates on mixing the alcoholic hydrochlorate with a moderately strong and neutral alcoholic solution of platinic chloride, as a dark yellow, bulky, flocculent precipitate, permanent in the air, and crystallising from alcohol of 75—80 per cent. by evaporation over oil of vitriol, in brown glassy crystals belonging to the regular system.

An alcoholic solution of the free base mixed with alcoholic *platinic chloride*, forms a bulky precipitate of the compound $C^{36}H^{30}N^2PtCl^4$. Analogous compounds are obtained with *mercuric chloride* and *silver-nitrate*.

The base $C^{18}H^{15}N$ above described is usually regarded as triphenylamine, but it has not been shown to yield by decomposition any compound of phenyl, or any of the usual products of decomposition of phenyl-compounds; and the mode of its formation seems rather to show that it is dicinnamylamine, $(C^9H^7)^2HN$. With *iodide of ethyl*, it yields the compound $C^{20}H^{20}NI = (C^2H^5)(C^6H^5)^3NI$ or $(C^2H^5)(C^9H^7)^2HNI$ (see phenylammonium).

**Tolylaniline, Benzylaniline, Phenyl-tolylamine** or **Phenyl-benzylamine.** $C^{13}H^{13}N = \left.\begin{matrix}C^6H^5\\C^7H^7\\H\end{matrix}\right\}N.$ (Hofmann, Ann. Ch. Pharm. cxxxii. 292.)—Produced by the dry distillation of a salt of tritolyl-rosaniline (toluidine-blue) in the same manner as diphenylamine is produced from triphenyl-rosaniline (p. 453). To prepare it, a solution of crystallised acetate of rosaniline in twice its weight of toluidine (benzylamine) is boiled for some hours in a flask having a vertical condensing tube; the blue mass is then distilled, and the distillate mixed with hydrochloric acid and then with water, whereby aniline and toluidine and other bases accompanying the phenyltolylamine are dissolved as hydrochlorates, while the phenyl-tolylamine remains as an oily layer, which usually solidifies or may easily be purified by rectification. The resulting crystals are finally recrystallised from alcohol.

Phenyl-tolylamine melts at 87° and boils 334·5 (corrected). It is much less soluble than diphenylamine. *Nitric acid* converts it into a blue substance scarcely distinguishable from that produced in like manner from diphenylamine. It unites with *acids* forming loosely combined compounds which are easily decomposed by contact with water, by heat, or even by evaporation in a vacuum. The *hydrochlorate*, $C^{13}H^{13}N.HCl$, obtained by adding concentrated hydrochloric acid to a concentrated alcoholic solution of the base, crystallises in laminæ.

Phenyltolylamine fused with *mercuric chloride*, forms a dark-coloured mass which dissolves in alcohol with splendid violet-blue colour, and probably consists of diphenyl-rosaniline, $C^{20}H^{17}(C^6H^5)^2N^3$.

Phenyl-tolylamine heated with *chloride of benzoyl*, forms phenyl-tolyl-benzamide) $(C^6H^5)(C^7H^7)(C^6H^4O)^2N$.

**Vinyl-aniline.** $C^8H^9N = (C^6H^5)(C^2H^3)HN$? *Acetyl-aniline.*—A base obtained together with other products, by the action of chloride of ethylene on aniline (Natanson, Ann. Ch. Pharm. xcviii. 297). It is probably identical with ethylene-phenylamine, $(C^2H^4)''(C^2H^5)N$ (see page 456, foot-note).

## b. Phenyl-diamines.

These are diatomic ammonias having 2 at. hydrogen replaced by phenyl, and 2 or 3 other hydrogen atoms by a di- or tri-atomic radicle.

Hofmann (Proc. Roy. Soc. ix. 277; x. 104), by acting upon aniline with dibromide of ethylene, obtained ethylene-diphenyldiamine and diethylene-diphenyldiamine, according to the equations:

$$2(C^6H^5.H^2.N) + C^2H^4Br^2 = (C^2H^4)''(C^6H^5)^2H^2N^2 + 2HBr.$$

$$2(C^6H^5.H^2.N) + 2C^2H^4Br^2 = (C^2\overset{\prime\prime}{H}{}^4)^2(C^6H^5)^2N^2 + 4HBr;$$

and Schiff (Ann. Ch. Pharm. Suppl. iii. 343), by treating aniline with acetic aldehyde (oxide of ethylidene), has obtained two compounds of the same composition as the preceding, but differing from them in physical properties, and related to them in the same manner as aldehyde to oxide of ethylene, and acetal to diethylate of ethylene, that is to say, containing ethylidene (ii. 598) instead of ethylene. Their formation may be represented by equations exactly similar to the preceding, substituting O for $Br^2$.

Compounds analogous to the second of these bases are likewise obtained by treating aniline with valerianic, œnanthylic, benzoic, and other aldehydes, the general equation of their formation being:

$$2\left[\left.\begin{matrix}C^6H^5\\H^2\end{matrix}\right\}N\right] + 2C^nH^{2n}O = \left.\begin{matrix}(\overset{\prime\prime}{C^n}H^{2n})^2\\(C^6H^5)^2\end{matrix}\right\}N^2 + 2H^2O.$$

A phenyl-diamine containing a triatomic radicle, viz. formyl-diphenyl-diamine, $(CH)'''(C^6H^5)^2HN^2$, is produced by the action of chloroform on aniline (Hofmann, Proc. Roy. Soc. ix. 230), thus:

$$2(C^6H^5.H^2.N) + CHCl^3 = (CH)'''(C^6H^5)^2HN^2 + 3HCl.$$

Griess (Ann. Ch. Pharm. cxxi. 257; Jahresb. 1862, p. 337), by passing nitrous acid into an alcoholic solution of aniline, has obtained azodiphenyldiamine, $C^{12}H^{11}N^3 = \left.\begin{matrix}(C^6H^5)^2\\ N'''\\ H\end{matrix}\right\}N^2$; and similar compounds are obtained by the action of nitrous acid on alcoholic solutions of bromaniline, chloraniline, and nitraniline.

Lastly, melaniline, $C^{13}H^{13}N^3$, may be regarded as cyano-diphenyl-diamine, $\left.\begin{matrix}CN\\ (C^6H^5)^2\\ H^3\end{matrix}\right\}N^2$, and the base $C^{19}H^{17}N^3$, produced by the action of tetrachloride of carbon on aniline, as cyano-triphenyl-diamine, $\left.\begin{matrix}CN\\ (C^6H^5)^3\\ H^2\end{matrix}\right\}N^2$.

### 1. *Ethylene-compounds.*

**Ethylene-diphenyl-diamine.** $C^{14}H^{16}N^2 = (C^2H^4)''(C^6H^5)^2H^2N^2$.—This compound is obtained by treating bromide of ethylene with a large excess of aniline (1 vol. of the former to 4 vol. of the latter). The mixture rapidly solidifies to a crystalline mass, from which water removes a considerable quantity of hydrochlorate of aniline, leaving a brown resinous substance, which gradually but imperfectly solidifies. This substance forms a hydrochlorate which dissolves but sparingly in strong hydrochloric acid, and may be readily purified by repeated crystallisation from boiling alcohol. On mixing the aqueous solution of this pure hydrochlorate with potash or ammonia, ethylene-diphenyl-diamine separates as an oil which quickly solidifies to a crystalline mass and may be purified by repeated crystallisation from dilute alcohol.

Ethylene-diphenyl-diamine is very soluble in *alcohol* and *ether*. It melts at 59°. With *hydrochloric* acid it forms the hydrochlorate, $C^{14}H^{16}N^2.2HCl$, or chloride of ethylene-diphenyl-diammonium, $(C^2H^4)''(C^6H^5)^2H^4N^2.Cl^2$, which when treated with *platinic chloride* yields the chloroplatinate, $(C^2H^4)''(C^6H^5)^2H^4N^2Cl^2.Pt^{iv}Cl^4$.

*Dibromide of ethylene* in presence of alcohol, converts it into diethylene-diphenyl-diamine:

$$(C^2H^4)''(C^6H^5)^2H^2N^2 + C^2H^4Br^2 = (C^2\overset{''}{H}{}^4)^2(C^6H^5)^2N^2 + 2HBr.$$

*Ethylene-diphenyl-diethyl-diamine*, $C^{18}H^{24}N^2 = (C^2H^4)''(C^6H^5)^2(C^2H^5)^2N^2$, is obtained, in combination with hydriodic acid, by digesting ethylene-diphenyl-diamine with iodide of ethyl for some hours at 100°. The *hydriodate*, $C^{18}H^{24}N^2.2HI$, or iodide of ethylene-diphenyl-diethyl-diammonium, $C^{18}H^{26}N^2I^2 = (C^2H^4)''(C^6H^5)^2(C^2H^5)^2H^2N^2.I^2$, then separates in well-defined prisms sparingly soluble in water, more soluble in alcohol. When treated with potash it yields the free base, $C^{18}H^{24}N^2$, which is also crystalline and melts at 70°. The *chloroplatinate*, $C^{18}H^{26}N^2Cl^2.Pt^{iv}Cl^4$, crystallises in needles.

**Diethylene-diphenyl-diamine.** $C^{16}H^{18}N^2 = (\overset{''}{C^2}H^4)^2(C^6H^5)^2N^2$.—This base is produced, as already observed, by the action of bromide of ethylene on ethylene-diphenyl-diamine; also, together with two others having the same percentage composition, by heating 1 vol. bromide of ethylene with 2 vol. aniline. It was at first regarded by Hofmann as *ethylene-phenylamine*, $(C^2H^4)''(C^6H^5)N$, but its deportment with the iodides of methyl and ethyl (p. 456) show it to be a diamine. It is polymeric, or metapolymeric, with the base called *vinyl-phenylamine*, which Natanson obtained by the action of dichloride of ethylene on aniline, and with *phthalidine*, $(C^{10}H^7)H^2N$ (?), which Dusart found among the products of decomposition of nitronaphthalene.

*Preparation.*—A mixture of 1 vol. bromide of ethylene and 2 vol. aniline exposed to the heat of boiling water for an hour or two, solidifies to a crystalline mass consisting of hydrobromate of aniline, together with three other bases, partly free, partly as hydrobromates. These bases are separated by their different degrees of solublity in alcohol, the first being extremely, the second but slightly soluble, and the third insoluble. To effect the separation, the solid mass is distilled with water to remove unaltered aniline and bromide of ethylene, and the residue is mixed with strong caustic potash, which sets free the portion of the bases combined with hydrobromic acid, in the form of a semisolid resin. This is washed with water and redistilled with water, whereby an additional quantity of unaltered aniline is expelled, and the residuary mass is treated with boiling spirit (methylated). The insoluble base is then left as a white powder, while the other two dissolve in the spirit, and the solution on cooling deposits crystals of the less

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soluble base, which is diethylene-diphenyl-diamine, and constitutes by far the largest part of the product, while the more soluble base remains in solution.* The diethylene-diphenyl-diamine may be purified by two or three crystallisations from alcohol.

*Properties.*—Diethylene-diphenyl-diamine crystallises in snow-white nacreous needles, tasteless, inodorous, insoluble in *water*, soluble in boiling, less soluble in cold *alcohol*, soluble in *ether*; the solutions are neutral to vegetable colours. It melts at 148°, and begins to boil and distil at 300°, the greater part undergoing decomposition and yielding considerable quantities of aniline, together with other products not examined.

The base dissolves easily in *hydrochloric*, *sulphuric*, and *nitric acid*, especially on gently heating the liquids, which on cooling deposit well crystallised salts. The *hydrochlorate*, $C^{16}H^{18}N^2.2HCl$ or $C^{16}H^{20}N^2Cl^2$, forms yellow precipitates with *auric* and *platinic chlorides*, the latter containing $C^{16}H^{20}N^2Cl^2.Pt^{iv}Cl^4$.

The base is not acted upon in any way by *bromide of ethylene*, even after prolonged contact at 100°—150°; but when heated for some time to 100° with the *iodides of methyl* and *ethyl*, it unites directly with them, yielding the compounds $C^{16}H^{18}N^2.CH^3I$ and $C^{16}H^{18}N^2.C^2H^5I$.

The *methyl-compound*, when freed from excess of methylic iodide by distillation with water, then washed with cold water and repeatedly crystallised from boiling water—mixed in the latter stages with a small quantity of spirit—is a crystalline yellowish compound which may be dried at 100° without decomposition. Oxide of silver converts it into a powerfully alkaline liquid resembling the solution of hydrate of tetrethylammonium, and yielding with hydrochloric acid and platinic chloride, a pale yellow amorphous *platinum-salt* containing $2(C^{16}H^{18}N^2.CH^3Cl).Pt^{iv}Cl^4$.

The *ethyl-compound*, $C^{16}H^{18}N^2.C^2H^5I$, is obtained in like manner, but requires longer digestion. It crystallises in yellowish-white needles which melt at 100° to a yellow oil. It is also decomposed by oxide of silver, yielding a strongly alkaline solution which forms with hydrochloric acid and platinic chloride the compound $2(C^{16}H^{18}N^2.C^2H^5Cl).Pt^{iv}Cl^4$.

### 2. *Ethylidene-compounds.*

By the action of acetic aldehyde on aniline, two bases are formed isomeric with the ethylene bases just described. At ordinary temperatures the action takes place with great violence, water being separated and a thick brown liquid formed. But if the two liquids before mixing are cooled by a mixture of ice and salt, and the aniline is kept in excess, a more moderate, though still very rapid action takes place, and the resulting mass has only a slight yellow colour. This product enclosed in a sealed tube and left to itself for some weeks, assumes a red colour which becomes darker on finally heating it to 100° for a few hours. On opening the tube, the water formed during the reaction (p. 454) is easily decanted from the thick liquid, and the latter, after being freed from excess of aniline by dilute acetic acid, may be further purified by washing it several times with water, dehydrating it in the fused state with chloride of calcium, then dissolving it in a considerable quantity of ether-alcohol to separate certain flocculent impurities, evaporating the solution in a retort, and drying the residue for some time between 100° and 110°.† The product thus obtained is a shining, ropy, slightly violet-coloured mass containing ethylidene- and diethylidene-diphenyl-diamine, which may be separated by boiling alcohol, the latter dissolving easily and abundantly therein, while the greater part of the former remains undissolved and the rest separates from the alcoholic solution on cooling.

**Ethylidene-diphenyl-diamine,** $C^{14}H^{16}N^2 = (C^2H^4)''(C^6H^5)^2H^2N^2$, is obtained by repeated crystallisation from hot alcohol in spherical groups of crystals always having a faint yellow colour; in the perfectly pure state, it would probably be colourless. When exposed to light and air it gradually turns reddish. It does not unite with the weaker acids, but readily with the stronger acids. The *sulphate*, *nitrate*, and *hydrochlorate* are so extremely soluble, even in alcohol, that they cannot be made to crystallise. The base deliquesces in hydrochloric acid gas. The acid solution of the hydrochlorate is precipitated by several metallic salts. With *mercuric chloride* it forms a yellow flocculent crystalline precipitate of the chloromercurate, $2(C^{14}H^{16}N^2.HCl)Hg''Cl^2$, which is insoluble in water, but dissolves in alcohol containing hydrochloric acid, forming a solution from which sulphydric acid throws down very finely divided mercuric sulphide. At 130° it turns red, begins to fuse, and gives off a large quantity of hydrochloric acid, leaving the compound $2C^{14}H^{16}N^2.Hg''Cl^2$.

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* The more soluble and the insoluble base have the same percentage composition as diethylene-diphenyl-diamine, but their rational formulæ have not been determined. It is probable, however, that the former is ethylene-phenylamine, $C^8H^9N = (C^2H^4)''(C^6H^5)N$, and the latter triethylene-triphenyltriamine, $C^{24}H^{27}N^3 = (C^2H^4)''^3(C^6H^5)^3N^3$. The former is probably also identical with Natanson's vinyl-phenylamine (p. 454).

† The same method serves for the purification of the products obtained by the action of other aldehydes upon aniline, to be described further on.

The *chloroplatinate*, $2(C^{14}H^{16}N^2.HCl).Pt^{iv}Cl^4$, is a yellowish-red crystalline precipitate insoluble in water, slightly soluble in alcohol.

**Diethylidene-diphenyl-diamine.** $C^{16}H^{18}N^2 = (C^2\overset{''}{H}{}^4)^2(C^6H^5)^2N^2$.—This base remains on evaporating the alcoholic solution above mentioned, as a red resinous mass, and may be obtained by repeated solution in alcohol, and repeated precipitation from acid solution, in solid but not in crystalline form. It may also be prepared by the action of aniline on oxychloride of ethylidene (ii. 599):

$$(C^2\overset{''}{H}{}^4)^2Cl^2O \quad + \quad 4C^6H^7N \quad = \quad (C^2\overset{''}{H}{}^4)^2(C^6H^5)^2N^2 \quad + \quad 2(C^6H^7N.HCl) \quad + \quad H^2O.$$

It differs from the monoethylidenated base in its inferior tendency to crystallise, but resembles it very closely in solubility and in its behaviour with acids. Its solution in hydrochloric acid gives with *platinic chloride*, an orange-coloured crystalline precipitate consisting of $2(C^{16}H^{18}N^2.HCl)Pt^{iv}Cl^4$, and with *mercuric chloride* a yellowish flocculent precipitate of the compound $2C^{16}H^{18}N^2.Hg''Cl^2$.

Both the ethylidene bases unite with *iodide of ethyl*, forming compounds probably similar in constitution to the ethylene-compounds already mentioned (p. 456). On heating 1 at. of the diethylidene-base with 2 at. ethylic iodide, a considerable portion of the latter remains uncombined, but the resulting compound does not crystallise well, and has not been analysed.

### 3. *Phenyl-diamines containing other Aldehyde-radicles.*

**Diallylidene-diphenyl-diamine.** $C^{18}H^{18}N^2 \quad \left.\begin{matrix}(C^3\overset{''}{H}{}^4)^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Produced by treating aniline with acroleïn. The action is very violent and requires to be moderated by a freezing mixture. The pungent odour of the acroleïn is instantly destroyed,* and the product, treated by the method of purification above described (p. 456), yields the diamine in the form of a yellow inodorous mass, which dries up to a varnish, and if it still retains a slight excess of aniline, assumes a fine red colour when dry. It is insoluble in water, slightly soluble in alcohol. Its salts have not been obtained in the crystalline state. The hydrochloric acid solution mixed with alcohol yields pulverulent precipitates with mercuric and platinic chloride. The *platinum-salt* gave by analysis 21·24 and 21·38 per cent. platinum, the formula $2(C^{18}H^{18}N^2.HCl)PtCl^4$, requiring 21·2 per cent.

**Diamylidene-diphenyl-diamine.** $C^{22}H^{30}N^2 = \left.\begin{matrix}(C^5\overset{''}{H}{}^{10})^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Produced by the action of valeraldehyde on aniline. The action is much less energetic than with acetic aldehyde; nevertheless it is attended with considerable rise of temperature and immediate separation of water. The product purified as above is a thick yellow oil having a bitter taste, insoluble in water, easily soluble in alcohol and ether. It does not unite with acids; the alcoholic solution mixed with hydrochloric acid and platinic chloride and evaporated, does not yield any platinum-salt. Heated with *iodide* and *bromide of ethyl*, it yields compounds having the consistence of turpentine.

Altogether this and the following compounds differ considerably in their properties from the ethylidene-diamines, occupying indeed an intermediate place between basic amines and acid amides, and perhaps approaching more nearly to the latter. Nevertheless their relation to the ethylidene bases and their capability of uniting with the iodides of ethyl and methyl, make it more convenient to regard them as amines.

**Dibenzylidene-diphenyl-diamine.** $C^{26}H^{22}N^2 = \left.\begin{matrix}(C^7\overset{''}{H}{}^6)^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—This compound was discovered by Laurent and Gerhardt (Compt. chim. 1850, p. 117), who called it *benzoylanilide*, and assigned to it the formula $C^{13}H^{11}N$. It is produced by the action of aniline on bitter almond oil. The two bodies act upon one another at ordinary temperatures, with separation of water, and the reaction may be completed by heating the mixture to 100° for a few hours. The product is a crystalline mass which may be purified by repeated crystallisation from hot alcohol or from alcohol and ether. It then forms crystalline plates, according to Laurent and Gerhardt; Schiff, however, obtained it only as a yellow crystalline mass. Laurent and Gerhardt found that it could be distilled without decomposition and was thus obtained quite colourless; but according to Schiff it is in great part decomposed by distillation.

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* A respirator moistened with a small quantity of aniline affords a very good protection against the intensely irritating vapours of acrolein. (Schiff.)

*Benzoin*, $C^{14}H^{12}O^2$, heated with aniline to 100°, yields, with separation of water, a product which appears to be identical with that obtained with bitter almond oil, but crystallises more readily from ether. (Schiff.)

Dibenzylidene-diphenyl-diamine is tasteless and inodorous, very fusible, insoluble in *water*, very soluble in *alcohol* and in *ether*. It dissolves in hot strong *hydrochloric acid*, and does not appear to be decomposed by boiling the solution; but is separated in its original state on addition of ammonia. It is not dissolved by *acetic acid*. By boiling with strong *nitric* or *sulphuric acid*, it is resolved into bitter almond oil and aniline. *Bromine* passed into the alcoholic solution throws down crystalline tribromaniline (Laurent and Gerhardt). It does not form a chloroplatinate. It unites, but slowly, with *iodide of ethyl*. When 1 at. of the diamine and 2 at. iodide of ethyl are heated together for two days in a sealed tube, a considerable portion of the latter remains undecomposed. According to Borodine (Ann. Ch. Pharm. cxi. 254), benzoyl-anilide, $C^{13}H^{11}N$, unites with 1 at. ethylic iodide, and the compound boiled with potash yields an alkaline mass which decomposes by distillation, yielding a strongly alkaline liquid. According to Schiff, however, the alkaline mass thus obtained is nothing but a mixture of the original substance with aniline, which passes over on distillation.

The diamine when exposed to the air, especially if moist, assumes a blue-green colour, and is ultimately converted into a coloured amorphous mass. A blue colour is also produced by heating its alcoholic solution with nitric acid or with mercuric or platinic chloride, also by heating it in sealed tubes with ammonia. As the diamine contains the radicles phenyl and benzylidene, the blue substance produced in these reactions is probably related to the aniline dyes (see APPENDIX TO PHENYLAMINES).

The neutral diamine obtained either by the action of bitter almond oil or of benzoin upon aniline, undergoes a remarkable change when kept for some months in sealed tubes at ordinary temperatures, or heated for about ten hours to 180° and at last to 200°. It is then converted without change of composition into a *basic* substance capable of forming salts with acids. The basic modification is a brown glassy substance much more soluble in alcohol than the original body, less crystallisable, and in contact with acids, immediately acquires a deep red colour. Its salts are sparingly soluble in water, easily in alcohol. The hydrochlorate gives precipitates with mercuric and platinic chloride. The *platinum-salt* contains 17·6 per cent. platinum, agreeing with the formula $2(C^{26}H^{22}N^2.HCl)PtCl^4$, which requires 17·5 per cent.

This basic diamine is related to the original compound in the same manner as the ethylene-bases to the ethylidene bases above described, or as emarine to hydrobenzamide; it may therefore be called dibenzylene- or ditoluylene-diphenyl-diamine. (Schiff.)

*Benzylidene-diethyl-diphenyl-diamine.* $C^{23}H^{26}N^2 = (C^7H^6)''(C^2H^5)^2(C^6H^5)^2N^2$.—Produced by the action of bitter almond oil on ethyl-aniline, generally in the form of a resin, which may be obtained in solid form by repeated separation from its metallic compounds. It is insoluble in water, sparingly soluble in alcohol, more soluble in ether. It does not form definite salts with acids, but its solution in hydrochloric acid gives a white precipitate with mercuric chloride, and yellow with platinic chloride, the latter containing 18·4 per cent. platinum, while the formula $2(C^{23}H^{26}N^2.HCl)PtCl^4$ requires 18·5 per cent.

This ethylated diamine shows a still greater tendency than the dibenzylidene compound to form a blue compound by oxidation. The somewhat concentrated alcoholic solution is dark red by transmitted and dark blue by reflected light.

**Diheptylidene-diphenyl-diamine.** $C^{26}H^{38}N^2 = \left.\begin{matrix}(C^7H^{14})^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Aniline and œnanthol act on one another at ordinary temperatures, producing a rise of temperature of 40°—50°. The product purified as above is a yellow, bitter, oily liquid which may be partially distilled without decomposition. It is not basic, not even forming a chloroplatinate. Nitric acid attacks it violently, forming a brown resin. Sulphuric acid quickly decomposes it, especially when heated, into œnanthol and sulphate of aniline. It unites with alcoholic iodides. When heated for some hours to 100° in a sealed tube with excess of *amylic iodide*, it yields a yellow viscous body containing 2·18 per cent. iodine, the formula $C^{26}H^{38}N^2.C^5H^{11}I$ requiring 22·05 per cent.

*Heptylidene-diallyl-diphenyl-diamine.* $C^{25}H^{34}N^2 = \left.\begin{matrix}(C^7H^{14})''\\(C^3H^5)^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Produced by the action of œnanthol on allylaniline:

$$2\left[\left.\begin{matrix}C^6H^5\\C^3H^5\\H\end{matrix}\right\}N\right] + C^7H^{14}O = \left.\begin{matrix}(C^7H^{14})''\\(C^3H^5)^2\\(C^6H^5)^2\end{matrix}\right\}N^2 + H^2O.$$

It is a yellow oily liquid having a bitter taste and a very strong odour of geraniums. It dissolves in strong sulphuric acid, and on addition of water, part of it separates unaltered, while the rest is decomposed, yielding œnanthol. It has no basic properties.

*Heptylidene-diethyl-diphenyl-diamine.* $C^{23}H^{34}N^2 = \left.\begin{matrix}(C^7H^{14})''\\(C^2H^5)^2\\(C^6H^5)^2\end{matrix}\right\}N^2$.—Produced by the action of œnanthol on ethylaniline. It is a yellow oil which turns brown when heated, and distils, with some decomposition, between 215° and 220°. It does not unite, either with acids or with chlorides.

*Action of Aniline on Cinnamic, Cuminic, and Salicylic Aldehydes.*—Aniline acts on cinnamic and cuminic aldehydes in the same manner as on those above mentioned, forming diamines which have no basic properties and do not combine with platinic chloride. The cinnamic compound is resinous; the cuminic compound is a thick oil. The resinous residue left in the distillation of cumin-oil is not affected by aniline.

Aniline likewise unites in a similar manner on salicylic aldehyde (salicylous acid), as observed some time ago by Schischkoff (Compt. rend. xlv. 272). The product is crystalline, and consists of diphenyl-salicyl-diamide or salicylanilide, $C^{26}H^{22}N^2O^2$, a compound polymeric with phenyl-benzamide $C^{13}H^{11}NO$. Its formation is represented by the equation: $2C^7H^6O + 2C^6H^7N = \left.\begin{matrix}(C^7H''^6O)^2\\(C^6H^5)^2\end{matrix}\right\}N^2 + 2H^2O$.

### 4. *Formyl-compound.*

**Formyl-diphenyl-diamine.** $C^{13}H^{12}N^2 = \left.\begin{matrix}(C^6H^5)^2\\(CH)'''\\H\end{matrix}\right\}N^2$.—(Hofmann, Proc. Roy. Soc. ix. 229.)—This compound is formed by the action of chloroform on aniline:

$$4C^6H^7N + CHCl^3 = C^{13}H^{12}N^2.HCl + 2(C^6H^7N.HCl).$$

Chloroform and aniline do not act on one another at ordinary temperatures, and scarcely at the heat of boiling water; but on exposing a mixture of the two liquids in sealed tubes to 180°—190° for ten or twelve hours, a hard brown crystalline mass is obtained, consisting chiefly of the hydrochlorates of aniline and formyl-diphenyl-diamine. To purify the latter, the brown crystalline mixture is triturated with water and washed on a filter, till the precipitate obtained by adding potash to the wash-water, which is at first oily and consists only of aniline, gradually exhibits a tendency to solidify and ultimately falls as a yellowish-white crystalline substance. The residue on the filter is then to be dissolved in warm (not boiling) water; the solution is filtered from a brown resinous substance, and precipitated by ammonia or potash; and the crystalline precipitate thus obtained is washed till free from alkali, and repeatedly crystallised from weak spirit.

Formyl-diphenyl-diamine forms a white crystalline powder, or sometimes minute scales, generally of a yellowish tint, arising from a trace of a yellow substance formed during the reaction, which adheres to it with great tenacity. It is insoluble in water, but dissolves readily in *alcohol* and *ether*, and is precipitated from hot solutions by water as a yellow oil which solidifies to a white crystalline mass on cooling. It is easily dissolved by *acids*, with many of which it forms crystalline salts. These salts are not very stable, their solutions, especially when heated, being always found to contain more or less aniline. With *potash* or *ammonia*, they yield a precipitate of the base. The *hydrochlorate* contains $C^{13}H^{12}N^2.HCl$; the *chloroplatinate* $2(C^{13}H^{12}N^2.HCl).PtCl^4$.

### 5. *Azophenyl-diamines.*

**Azo-diphenyl-diamine.** $C^{12}H^{11}N^3 = \left.\begin{matrix}(C^{12}H^7N''')''\\H^4\end{matrix}\right\}N^2 = \left.\begin{matrix}(C^6H^5)^2\\N'''\\H\end{matrix}\right\}N^2$. (Griess, Ann. Ch. Pharm. cxxi. 257; Jahresb. 1862, p. 338; Phil. Trans. 1864, [3], 678.)—This compound, which contains the elements of aniline and azophenylamine (p. 431), and is accordingly regarded by Griess as *diazo-amidobenzene*, $C^6H^4N^2.C^6H^4(NH^2)$, is produced:—1. By the direct action of aniline on salts of azophenylamine, the nitrate for example.—2. By the action of aqueous aniline-salts on the compound of azophenylamine with hydrate of potassium: *e.g.*

$$C^6H^4N^2.KHO + C^6H^7N.HCl = C^{12}H^{11}N^3 + KCl + H^2O.$$

3. By the action of nitrous acid on an alcoholic solution of aniline:

$$2C^6H^7N + NHO^2 = C^{12}H^{11}N^3 + 2H^2O.$$

To prepare it by the last mentioned reaction, nitrous acid gas is slowly passed into a cooled solution of aniline in 6 to 10 pts. alcohol, till a small portion of the solution leaves on evaporation an oily residue, which solidifies to a crystalline resin, or till this residue begins to be insoluble in dilute acetic acid. The brown-red alkaline solution contains, together with azodiphenyl-diamine, variable quantities of phenol, benzene, nitrate and nitrite of aniline, and nitrate of azophenylamine (p. 431), formed by the further action of the nitrous acid on the azodiphenyl-diamine. On mixing the alcoholic solution with a large quantity of water, the diamine separates as an oily mass which afterwards solidifies, sometimes in yellow crystals. It may be freed from the mother-liquor containing the other substances just mentioned, by pressure and washing with cold water, and further purified by several recrystallisations from hot alcohol.

Azodiphenyl-diamine crystallises in golden-yellow shining laminæ, or less frequently in needles. It is tasteless and inodorous, insoluble in water, sparingly soluble in cold, more soluble in hot alcohol, and soluble in all proportions in ether. It melts at 91° to a red-brown oil, which solidifies again in the crystalline state at 50°; at a higher temperature it decomposes, and if in large quantity, explodes violently at about 200°. It is insoluble in the weaker acids, and is easily decomposed by strong acids, with evolution of nitrogen. It is only towards platinic chloride and nitrate of silver that it exhibits any basic character. The *platinum-salt*, $2(C^{12}H^{11}N^3.HCl).PtCl^4$, separates on mixing the alcoholic solution of the base with an acid solution of platinic chloride, in small reddish needles or prisms, nearly insoluble in alcohol, ether, and water, easily decomposible, detonating when strongly heated. With *nitrate of silver* the diamine forms a greenish-yellow precipitate, agreeing approximately with the formula $C^{12}H^{11}N^3.NAgO^3$.

Azodiphenyl-diamine, heated with strong *hydrochloric acid*, under a layer of ether, is resolved into phenol, hydrochlorate of aniline, and free nitrogen:

$$C^{12}H^{11}N^3 + H^2O + HCl = C^6H^6O + C^6H^7N.HCl + N^2.$$

With *bromine* in ethereal solution it forms hydrobromate of azophenylamine, which separates out, and tribromaniline, which remains in the mother-liquor and afterwards crystallises in white needles:

$$C^{12}H^{11}N^3 + Br^6 = C^6H^4N^2.HBr + C^6H^4Br^3N + 2HBr.$$

Bromopicrin is also formed as a secondary product. When the diamine, dissolved in a mixture of alcohol and ether, is treated with nitric acid containing *nitrous acid*, nitrate of azophenylamine is formed, and separates in white crystals:

$$C^{12}H^{11}N^3 + NHO^2 + 2NHO^3 = 2(C^6H^4N^2.NHO^3) + 2H^2O.$$

***Azo-bromodiphenyl-diamine***, $C^{12}H^9Br^2N^3 = \left.\begin{matrix}(C^6H^4Br)^2\\ N'''\\ H\end{matrix}\right\}N^2$, or *Diazoamido-bromobenzene*, $C^6H^3BrN^2.C^6H^4Br(NH^2)$.—Produced by the action of bromaniline on nitrate of azophenylamine (or azobromophenylamine) or of nitrous acid on an alcoholic solution of bromaniline, and purified like the preceding. It exhibits the same properties whether prepared from α- or β-bromaniline. It forms yellowish-red highly lustrous laminæ and needles, very soluble in ether, and melting at 145°. In other respects it resembles azodiphenyldiamine. The *platinum-salt*, $C^{12}H^9Br^2N^3.H^2Cl^2.PtCl^4$, forms buff-coloured capillary crystals, which deflagrate easily and are nearly insoluble in water and ether. *Nitrate of silver* added to the alcoholic solution forms a yellow precipitate of the salt $C^{12}H^9Br^2N^3.NAgO^3$. (Griess, *loc. cit.*)

***Azo-dibromodiphenyl-diamine***, $C^{12}H^7Br^4N^3 = \left.\begin{matrix}(C^6H^3Br^2)^2\\ N'''\\ H\end{matrix}\right\}N^2$, or *Diazo-amido-dibromo-benzene*, $C^6H^7Br^2N^2.C^6H^3Br^2(NH^2)$, is obtained in like manner by the action of nitrous acid on alcoholic dibromaniline, as a bulky yellow precipitate consisting of a network of interlaced microscopic needles. It is but very slightly soluble, and usually crystallises from alcohol or ether in small golden-yellow needles, melting at 167·5°, sometimes in yellow-brown granules, or yellow or ruby-red well-developed prisms, which latter however are converted by recrystallisation into the golden-yellow needles. (Griess, *loc. cit.*)

***Azo-chlorodiphenyl-diamine***, $C^{12}H^9Cl^2N^3 = \left.\begin{matrix}(C^6H^4Cl)^2\\ N'''\\ H\end{matrix}\right\}N^2$, or *Diazoamido-chlorobenzene*, $C^6H^3ClN^2.C^6H^4Cl(NH^2)$, obtained like the corresponding bromine-compound, forms yellow needles or laminæ melting at 124·5°.

***Azo-dichlorodiphenyldiamine***, $C^{12}H^7Cl^4N^3 = \left.\begin{matrix}(C^6H^3Cl^2)^2\\ N'''\\ H\end{matrix}\right\}N^2$ or *Diazoamido-*

*dichlorobenzene*, $C^6H^3Cl^2N^2.C^6H^3Cl^2(NH^2)$.—Produced by the action of nitrous acid on alcoholic dichloraniline, crystallises in light sulphur-yellow, capillary needles, melting at 126·5°, insoluble in water, very slightly soluble in hot alcohol or ether. Like the corresponding bromine-compound, it does not form a platinum-salt, but rather behaves like an acid, being soluble without decomposition in caustic potash. (Griess, *loc. cit.*)

*Azo-nitrodiphenyl-diamine*, $C^{12}H^9N^5O^4 = \left.\begin{matrix}[C^6H^4(NO^2)]^2\\ N'''\\ H\end{matrix}\right\}N^2$, or *Diazoamido-nitrobenzene*, $C^6H^4(NO^2)N^2.C^6H^4(NO^2)(NH^2)$.—Produced by the action of nitrous acid on an alcoholic solution of α- or β-nitraniline,* and exhibits corresponding isomeric modifications. The α-compound is insoluble in water, very sparingly soluble in alcohol and ether, and crystallises from either of these solvents in ruby-red or reddish-yellow prisms, mostly well-defined. It melts at 195·5°.

The β-compound is precipitated as a yellow crystalline mass consisting of an aggregate of granular or moss-like microscopic crystals. It is insoluble in water, very sparingly soluble in alcohol or ether, melts at 224·5° to a reddish-brown oil, and detonates at a higher temperature. It is almost wholly indifferent, not forming a compound even with chloride of platinum. With an alcoholic solution of *silver-nitrate*, however, it forms a yellowish-green amorphous precipitate. (Griess, *loc. cit.*)

**Azo-phenyl-naphthyl-diamine.** $C^{16}H^{13}N^3 = \left.\begin{matrix}(C^6H^5\\ N'''\\ H\\ C^{10}H^7\end{matrix}\right\}N^2$. (Griess, Phil. Trans. 1864, [3], 679.)—This compound contains the elements of azophenylamine and naphthylamine, and is regarded by Griess as *diazobenzene-amidonaphthalene*, $C^6H^4N^2.C^{10}H^7(NH^2)$. It is obtained as a nitrate in the form of a violet crystalline precipitate by adding an aqueous solution of nitrate of azophenylamine to an alcoholic solution of naphthylamine:

$$C^6H^4N^2.NHO^3 \quad + \quad C^{10}H^9N \quad = \quad C^{16}H^{13}N^3.NHO^3.$$

The nitrate purified by repeated washings with cold alcohol and recrystallisation from hot alcohol, forms well-defined prisms of a magnificent grass-green colour by transmitted, but ruby-red by reflected light. It is almost insoluble in water and ether, but dissolves freely in hot alcohol and separates almost wholly on cooling.

The nitrate decomposed by ammonia or potash yields the free base, which crystallises in very brilliant ruby-red prisms, easily soluble in alcohol and ether, forming yellow solutions to which acids impart a beautiful violet colour. With *platinic chloride* it forms a purple-blue crystalline precipitate, and with *nitrate of silver*, a yellow precipitate composed of small fine needles.

### 6. *Cyanophenyl-diamines.*

There are two derivatives of aniline which may be classed under this head, namely cyano-diphenyl-diamine, or melaniline, produced by the action of chloride of cyanogen on aniline, and cyano-triphenyl-diamine, by the action of tetrachloride of carbon on aniline. The latter, however, is more probably a triamine, and will be described under that head (p. 465).

**Cyano-diphenyl-diamine or Melaniline,** $C^{13}H^{13}N^3 = C^6H^5CyN.C^6H^7N = \left.\begin{matrix}(C^6H^5)^2\\ CN\\ H^3\end{matrix}\right\}N^2$, might also be represented as carbo-diphenyl-diamine, $\left.\begin{matrix}(C^6H^5)^2\\ C^{iv}\\ H^3\end{matrix}\right\}N^3$. (Hofmann, Ann. Ch. Pharm. lxvii. 129; lxxiv. 8 and 17.)—This compound, which contains the elements of 1 at. aniline and 1 at. cyanophenylamine (cyanilide), is produced by the action of chloride or bromide of cyanogen on anhydrous aniline. As cyanophenylamine is produced by the action of chloride of cyanogen on aniline dissolved in anhydrous ether (p. 442), it is probable that, in the reaction now under consideration, cyanophenylamine is also produced in the first instance and immediately unites with a molecule of free aniline forming melaniline.

*Preparation.*—When gaseous chloride of cyanogen (obtained by the action of chlorine on moist cyanide of mercury) is passed into aniline, the gas is absorbed, with great rise of temperature, while the liquid acquires a darker colour and thickens to a crystalline mass. This mass is to be heated till the crystals melt, so that it may be completely saturated with chloride of cyanogen; the clear brownish, non-crystalline, resinous mass, which is produced on cooling and consists of hydrochlorate of melaniline (together with a brown oil insoluble in hydrochloric acid, which forms in greater quantity as the chloride of cyanogen is more humid, and not at all if the gas has been previously passed over chloride of calcium), is dissolved in water, the solution being accelerated by addition of hydrochloric acid and boiling; the liquid filtered from the oil is precipitated by potash; and the white viscid precipitate, which immediately solidifies in the crystalline form (only after some time, however, if it contains undecomposed aniline), is washed with cold water, till the whole of the chloride of potassium is removed, and purified by two crystallisations from a mixture of equal parts of alcohol and water, which yields the finest crystals.

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* See foot-note, p. 445.

*Properties.*—Melaniline forms white, hard, easily friable laminæ and broad needles, which float on water, but sink in the fused state, and between 120° and 130°, melt into a slightly coloured oil, which solidifies in a crystalline mass on cooling. It is inodorous, but has a bitter persistent taste; slightly blues reddened litmus, but does not change the colour of turmeric; it acquires a reddish tint when exposed to the air. It dissolves sparingly in cold, more easily in boiling *water*, and separates in small scales on cooling. It is easily soluble in *alcohol*, *ether*, *wood-spirit*, *acetone*, *sulphide of carbon*, and *oils* both fixed and volatile.

*Decompositions.*—1. Melaniline begins to decompose between 150° and 170°, giving off aniline and ammonia.—2. *Chlorine*-water added in very large excess to hydrochlorate of melaniline, completely precipitates the base in the form of a resinous mass probably consisting of trichloromelaniline. If the chlorine-water be gradually added, till the turbidity thereby produced no longer disappears on agitation, the liquid filtered from the resinous precipitate contains hydrochlorate of dichloromelaniline. —3. When *bromine* is added to aqueous hydrochlorate of melaniline in the manner just described with reference to chlorine-water, the filtrate deposits, on evaporation, needles of hydrochlorate of dibromomelaniline; and the mother-liquor mixed with a larger quantity of bromine and evaporated, yields transparent, yellow, oily drops which crystallise on cooling, and probably consist of tribromomelaniline; Bromine acting in excess on hydrochlorate of melaniline forms a resinous substance still richer in bromine.—4. Alcoholic *iodine* added in excess to hydrochlorate of melaniline, throws down nearly the whole as a black viscid mass, which when the quantity of iodine is less, is precipitated in smaller amount, while undecomposed melaniline remains in solution.—5. Fuming *nitric acid* suddenly mixed with an equal quantity of melaniline, produces great heat, rising even to explosion, attended with slight fuming; and, when gradually added, produces, according to the duration of the action, orange-yellow crystals of an alkaloïd with violet iridescence, and lemon-yellow prisms of an acid which forms scarlet salts with alkalis. Moderately strong nitric acid added in great excess or heated, likewise exerts a decomposing action.—6. *Cyanogen gas* passed through an alcoholic solution of melaniline, is abundantly absorbed; and the liquid, if then inclosed in a bottle, deposits dicyanomelaniline, the odour of cyanogen changing at the same time into that of hydrocyanic acid, while the brown mother-liquor contains other products of decomposition.

Salts of Melaniline.—Melaniline is but a weak base, and does not precipitate ferric salts. It dissolves in acids very readily and with slight evolution of heat, and neutralises them completely. The salts are colourless or slightly coloured, mostly crystallisable, and taste very bitter; with firwood, chloride of lime and chromic acid, they do not exhibit the colouring produced by aniline-solutions. They are precipitated by ammonia and more completely by potash or soda (also by the carbonates, with evolution of carbonic acid, yielding a white, quickly crystallising precipitate), but not by aniline; neither does melaniline precipitate the aniline-salts.

*Hydriodate of Melaniline.* $C^{13}H^{13}N^3.HI$.—Concentrated hydriodic acid converts melaniline into an oil, which sinks to the bottom and gradually solidifies in a crystalline mass. It decomposes quickly on exposure to the air, with liberation of iodine. From a solution in boiling water, it separates on cooling in oily drops which afterwards solidify. It dissolves also in alcohol.

*Hydrobromate of Melaniline.* $C^{13}H^{13}N^3.HBr$.—Crystallises from water in stellate groups of needles very soluble in water, less soluble in strong hydrobromic acid.

*Hydrochlorate.*—The aqueous solution does not yield crystals by spontaneous evaporation; when dried over oil of vitriol or in the water-bath, it dries up to a clear, slightly coloured gum, which crystallises very slowly. It is the most soluble in water of all the salts of melaniline. A moderately concentrated solution of this salt mixed with trichloride of gold becomes turbid after a while, and deposits fine golden-yellow needles of the *chloroaurate*, $C^{13}H^{13}N^3.HCl.AuCl^3$. With a concentrated solution of the hydrochlorate an immediate precipitate is formed. The chloroaurate is but slightly soluble in water. Platinic chloride forms with hydrochlorate of melaniline a light yellow slightly crystalline precipitate of the *chloroplatinate*, $2(C^{13}H^{13}N^3.HCl).PtCl^4$, and the filtered liquid deposits, after some time, orange-coloured crystals having the same composition. The platinum-salt dissolves in a small quantity of boiling water; it is less soluble in alcohol, insoluble in ether. *Mercuric chloride* forms in solutions of aniline a white precipitate easily soluble in hydrochloric acid, and forming a solution which deposits needles by spontaneous evaporation.

*Hydrofluate.*—The solution of melaniline in weak hydrofluoric acid yields well developed crystals, having a faint reddish colour, somewhat soluble in water, less soluble in alcohol.

*Nitrate of Melaniline.* $C^{13}H^{13}N^{3}.NHO^{3}$.—Crystallises on cooling from the hot aqueous solution so completely, that the mother-liquor is but slightly clouded by potash, and not by ammonia. The needles assume a faint reddish tint by exposure to the air, but are otherwise permanent. They dissolve also in hot alcohol, but are nearly insoluble in ether.

*Argento-nitrate of Melaniline,* $2C^{13}H^{13}N^{3}.NAgO^{3}$, is precipitated immediately on mixing the alcoholic solution of melaniline with aqueous nitrate of silver, as a white mass, which quickly agglutinates to a resin, and must be purified from free melaniline by trituration with alcohol; from a clear alcoholic mixture of melaniline and nitrate of silver, the salt separates after a few hours in hard crystalline geodes.

*Oxalate of Melaniline.* $C^{13}H^{13}N^{3}.C^{2}H^{2}O^{4}$.—Melaniline forms crystals with excess of oxalic acid. These crystals melt when heated, give off, with violent ebullition, equal volumes of carbonic oxide and carbonic anhydride, smelling strongly of anilocyanic acid, yield a distillate of aniline and a beautiful crystalline sublimate of diphenyl-carbamide, and leave a clear viscid mass, which on cooling solidifies to a resin. The salt dissolves sparingly in cold water or alcohol, readily in boiling water or alcohol, but is nearly insoluble in ether.

The *phosphate* is very soluble in water and crystallises but slowly.

The *sulphate,* $2C^{13}H^{13}N^{3}.SH^{2}O^{4}$, forms stellate groups of rhombic plates, sparingly soluble in cold, freely in hot water; soluble also in alcohol and ether. Melaniline added to *sulphate of copper* throws down a flocculent double salt.

**DIBROMOMELANILINE.** $C^{13}H^{11}Br^{2}N^{3}$. (Hofmann, Ann. Ch. Pharm. lxvii. 148; Chem. Soc. Qu. J. i. 299.)—An aqueous solution of hydrochlorate of melaniline mixed with bromine in small portions, till the turbidity begins to be permanent, yields, when filtered, evaporated, and cooled, stellate groups of hydrobromate of dibromomelaniline, which, when dissolved in water, form with ammonia a white crystalline precipitate, crystallising from hot alcohol in white scales. The base tastes very bitter in its solutions. When heated above its melting point, it gives off pure bromaniline in the form of a colourless distillate, which solidifies in a yellowish crystalline mass, leaving a resinous mass similar to the residue obtained in the distillation of melaniline. It is nearly insoluble in water, but dissolves in alcohol and ether.

Its *hydrochlorate,* $C^{13}H^{11}Br^{2}N^{3}.HCl$, crystallises in white silky needles grouped in stars. These crystals, when immersed in a small quantity of boiling water, melt into an oil which solidifies in the crystalline form on cooling; they dissolve sparingly in water.

The hot saturated solution of the hydrochlorate forms with *platinic chloride* an orange-yellow precipitate, which on cooling crystallises in golden-yellow scales, nearly insoluble in water, sparingly soluble in ether, somewhat more in alcohol, and containing $2(C^{13}H^{11}Br^{2}N^{3}.HCl).PtCl^{4}$. (Hofmann.)

**DICHLOROMELANILINE.** $C^{13}H^{11}Cl^{2}N^{3}$. (Hofmann, *loc. cit.*)—When chlorine-water is gradually added to hydrochlorate of melaniline, till the turbidity no longer disappears on agitation, the filtrate when evaporated and cooled, yields hydrochlorate of dichloromelaniline in white stellate needles, or by further evaporation, as a yellowish oil which solidifies in the crystalline form. From the solution of this salt in water, in which it is but sparingly soluble (whereas it dissolves more readily in alcohol and still more in ether), ammonia precipitates the base in snow-white flakes, which separate from the alcoholic solution in hard crystalline laminæ.

*Platinum-salt,* $2(C^{13}H^{11}Cl^{2}N^{3}.HCl).PtCl^{4}$.—The hydrochlorate mixed with tetrachloride of platinum, yields an orange-yellow crystalline powder which must be washed with ether.

The resinous mass precipitated by mixing hydrochlorate of melaniline with a very large excess of chlorine water, which hardens after a while into an amorphous solid, exhibits a neutral reaction, and is insoluble in water hot soluble in alcohol, is probably trichloromelaniline, $C^{26}N^{3}Cl^{3}H^{10}$. (Hofmann.)

**DINIODOMELANILINE.** $C^{13}H^{11}I^{2}N^{3}$. (Hofmann, Ann. Ch. Pharm. lxvii. 152; Chem. Soc. Qu. J. i. 303.)—When chloride of cyanogen is passed through an ethereal solution of iodaniline, a crystalline precipitate of hydrochlorate of iodaniline is first formed, but if the passage of the gas be continued, the crystals disappear and the entire mass changes into a transparent resin of hydrochlorate of diniodomelaniline, which slowly becomes crystalline. From this compound, potash throws down the base in the form of a white body, which crystallises indistinctly from alcohol.

The *hydrochlorate* dissolves sparingly in water and separates from the boiling solution on cooling in oily drops, which very slowly change into white crystalline stars. The *chloroplatinate* is not very crystalline.

DINITROMELANILINE. $C^{13}H^{11}N^{5}O^{4} = C^{13}H^{11}(NO^{2})^{2}N^{3}$. (Hofmann, Ann. Ch. Pharm. lxvii. 156; Chem. Soc. Qu. J. i. 305.)—This base, like other nitro-derivatives of aniline, is susceptible of two isomeric modifications: α. produced by the action of chloride of cyanogen on α-nitraniline; β. by the action of fuming nitric acid on melaniline. The two modifications closely resemble one another in physical and chemical properties; but when distilled with potash, the former yields α-, the latter β-nitraniline.

*Preparation of α-nitromelaniline.*—Gaseous chloride of cyanogen is passed through a solution of α-nitraniline till the ether is nearly evaporated; the remaining crystalline mixture of undecomposed nitraniline, hydrochlorate of dinitromelaniline, and indifferent yellowish needles, is heated, with gradual addition of water, till the mass, which at first melts into a brown oil, is almost entirely dissolved; the liquid is cooled till the yellowish needles separate; the colourless filtrate containing hydrochlorate of dinitromelaniline is mixed with ammonia, which throws down the dinitromelaniline, as a quickly crystallising sulphur-yellow mass; and this precipitate is freed from nitraniline, with which it is generally mixed, by boiling with water.

*Properties.*—Nitromelaniline precipitated by ammonia or potash forms a scaly crystalline mass, of a much paler yellow colour than nitraniline; when precipitated from alcohol by water, it forms a golden-yellow crystalline mass, and short flat microscopic needles; from ether by spontaneous evaporation it crystallises in larger needles. It is insoluble in water even at the boiling heat, sparingly soluble in *alcohol*, still less in *ether*. When heated, it gives off a yellow vapour which condenses in brown oily drops chiefly consisting of nitraniline, and gradually crystallising, and leaves a brown resinous mass.

*Hydrochlorate of Dinitromelaniline*, $C^{13}H^{11}(NO^{2})^{2}N^{3}.HCl$, crystallises in flat shining needles, sparingly soluble in water. The *chloroplatinate*, $2[C^{13}H^{11}(NO^{2})^{2}N^{3}.HCl]PtCl^{4}$, is a yellow crystalline precipitate which is sparingly soluble in water and alcohol, insoluble in ether, and burns with a slight deflagration when heated. The *nitrate* is sparingly soluble. The *oxalate* forms easily soluble crystalline grains. The *sulphate* forms white crusts which dissolve easily in water.

**Dicyanomelaniline.** $C^{15}H^{13}N^{5} = C^{13}H^{13}N^{3}.Cy^{2}$. (Hofmann, Ann. Ch. Pharm. lxxvii. 100; lxxiv. 1).—A saturated solution of melaniline in cold alcohol absorbs a large quantity of cyanogen, and if the liquid be then left to itself in a closed vessel for some hours, solidifies to a crystalline pulp which may be purified by washing with alcohol and recrystallisation from boiling alcohol.

The product is dicyanomelaniline; it forms yellowish needles not volatile without decomposition; when heated it gives off aniline and cyanide of ammonium, and leaves a resinous residue which chars at higher temperature.

Dicyanomelaniline dissolves in cold dilute acids, and if potash or ammonia be immediately added to the solution, the dicyanomelaniline separates out unaltered; but it decomposes by prolonged contact with acids, so that it does not easily yield salts. Its solution in hydrochloric acid becomes turbid in a few minutes, and deposits a yellowish confusedly crystalline mass of melanoximide (p. 286) the mother-liquor retaining sal-ammoniac in solution:

$$\underset{\text{Dicyanomel-aniline.}}{C^{15}H^{13}N^{5}} + 2H^{2}O = \underset{\text{Melanoximide.}}{C^{15}H^{11}N^{3}O^{2}} + 2NH^{3}.$$

### C. Phenyltriamines.

These are bases derivable from a triple molecule of ammonia, $H^{9}N^{3}$, by the substitution of one or more atoms of phenyl for an equal number of hydrogen-atoms, and of a polyatomic radicle for a number of hydrogen-atoms corresponding to its atomicity. At present, however, there is but a small number of compounds known which can be referred to this class.

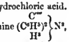
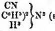
1. *Carbotriphenyl-triamine*, $C^{19}H^{17}N^{3} = \left.\begin{matrix} C^{iv} \\ (C^{6}H^{5})^{3} \\ H^{2} \end{matrix}\right\} N^{3}$. (Hofmann, Proc. Roy. Soc. ix. 284.)—This base is produced by the action of tetrachloride of carbon on aniline:

$$3(C^{6}H^{5}.H^{2}.N) + CCl^{4} = \left.\begin{matrix} C^{iv} \\ (C^{6}H^{5})^{3} \\ H^{2} \end{matrix}\right\} N^{3} + 4HCl.$$

It might also be formulated as *cyano-triphenyl-diamine* $\left.\begin{matrix} CN \\ (C^{6}H^{5})^{3} \\ H^{2} \end{matrix}\right\} N^{2}$; but its mode of formation shows it rather to be a triamine.

*Preparation.*—Aniline and tetrachloride of carbon do not act upon one another at ordinary temperatures, and but very slowly at 100°; but when a mixture of 3½ pts. aniline and 1 pt. of the tetrachloride, both in the anhydrous state, is heated to 170° in sealed tubes for about thirty hours, the liquid is converted into a black mass which adheres firmly to the sides of the tubes and is a mixture of several bodies. Water dissolves a portion of it, leaving a more or less solid resin, and the aqueous solution yields, on addition of potash, an oily precipitate containing a considerable portion of unchanged aniline. On boiling this precipitate with dilute potash in a retort, the aniline distils over, while a viscid mass remains behind which gradually solidifies with a crystalline structure. Washing with cold alcohol and two or three crystallisations from boiling alcohol render this body perfectly white and pure, while a very soluble substance of a splendid crimson colour remains in solution. The portion of the black mass which is insoluble in water dissolves almost entirely in dilute hydrochloric acid, from which solution it is precipitated by alkalis, as an amorphous pink or dingy-coloured precipitate soluble with rich crimson colour in alcohol. The greater part of this body consists of the same colouring principle that accompanies the white crystalline substance. Considerable quantities of this crystalline body are also occasionally present in the product insoluble in water.

The crystalline substance is **carbotriphenyl-triamine.** It is insoluble in water, difficultly soluble in *alcohol*, soluble in *ether*. From the hot alcoholic solution it crystallises slowly on cooling in elongated four-sided plates often grouped round a common centre. It dissolves freely in *acids*, from which it is thrown down by alkalis as a dazzling white precipitate. The *hydrochlorate*, $C^{19}H^{17}N^3.HCl$, and the *chloroplatinate*, $2(C^{19}H^{17}N^3.HCl).PtCl^4$, are extremely soluble in excess of hydrochloric acid.

2. **Melaniline,** $C^{13}H^{13}N^3$, may be regarded as carbo-diphenyl-triamine  $\left.\begin{matrix}C''''\\(C^6H^5)^2\\H^3\end{matrix}\right\}N^3$, but the mode of formation renders it more probable that this body really consists of cyano-diphonyl-diamine,  $\left.\begin{matrix}CN\\(C^6H^5)^2\\H^3\end{matrix}\right\}N^2$ (see p. 461).

3. **Rosaniline,** $C^{20}H^{19}N^3$, and some of the colouring matters derived from it are probably also triamines; but their rational formulæ still remain to be determined.

### *Appendix to Phenylamines.*

### Aniline-dyes.

The colorific tendencies of aniline have long been known. The violet-blue reaction with chloride of lime, which is the ordinary laboratory test for aniline, was discovered by **Runge** in 1835. Some years afterwards, **Fritzsche** showed that aniline treated with aqueous chromic acid yields a blackish-blue precipitate. **Beissenhirtz** in 1853 noticed the blue colour resulting from admixture of aniline with strong sulphuric acid and acid chromate of potassium; and the substance producing this blue coloration was isolated in 1856 by Mr. W. H. **Perkin**, who showed that it is a colouring matter capable of being fixed upon fabrics, and thus laid the foundation of the vast industry of aniline colours. Soon afterwards reds of various shades were obtained on the manufacturing scale by heating aniline with tetrachloride of tin, arsenic acid and various metallic salts, and a great number of other dyes, yellow, green, blue, violet, &c., have been obtained either by treating aniline-red with various reagents, or as secondary products in its preparation. A few have also been obtained by other processes.

**Aniline-black.** Blacks of great intensity are produced on calico by printing with a mixture of aniline, chlorate of potassium and a metallic salt. In 1863 Mr. **Lightfoot** of Accrington patented in France a method of producing aniline-black by printing with a mixture of 25 grms. chlorate of potassium, 50 grms. aniline, 50 grms. hydrochloric acid, 50 grms. cupric chloride, 25 grms. sal-ammoniac, 12 grms. acetic acid, and 1 litre of starch-paste, then exposing the cloth to the air for two days, and fixing the colour with an alkali. The black thus produced is very good and durable, but the process has not been much used, because the large quantity of copper in the mixture is found to corrode the steel scrapers or "doctors" of the printing machine, and moreover the large quantity of acid in the aniline-salt and in the copper-salt, causes a rapid destruction of the vegetable fibre.

Several methods of obviating these defects have been proposed; the best appears to be that of **Lauth**, which consists in replacing the soluble copper-salt by an insoluble compound, the sulphide for example. This compound, when printed together with the chlorate of potassium and hydrochlorate of aniline, is gradually oxidised by the action of the hypochlorous acid or of chlorine (set free by the mutual action of the salts just mentioned) and converted into sulphate, so that a mixture is formed similar to that used in Lightfoot's process. As however there is no excess of soluble copper salt, or of acid present, no corrosion of the scrapers or rollers, or destruction of the vegetable fibre need be feared.

Aniline-black thus produced has a very deep colour and rich velvety aspect. It is said to be very fast, quite insoluble in water, boiling soap-ley, alkalis and acids. The latter turn it green, but alkalis restore the original tint. Acid chromate of potassium deepens the colour; but a strong solution makes it slightly rusty. It is destroyed by a strong solution of chloride of lime, but reappears after some time with its original depth. The colour is capable of withstanding all the processes employed for the production of rose and red madder colours. (Bull. Soc. Chim. [2] ii. 416.)

**Aniline-blue.** Blue colouring matters are produced from aniline under the influence of various reagents, as by chlorate of potassium and hydrochloric acid, chlorous acid, peroxide of hydrogen (Lanth), ferric chloride, ferricyanide of potassium (E. Kopp, *Examen des Matières colorantes artificielles*, p. 68), hydrochloric acid and peroxide of manganese, ferric nitrate and hydrochloric acid (Scheurer-Kestner, *ibid.* p. 66). Products of this kind have been more especially studied by Calvert, Lowe, and Clift, who have described them under the name of azurine.

A much finer and more permanent blue, now designated especially as aniline-blue, is obtained by heating a salt of rosaniline (aniline-red) with excess of aniline. This colouring matter has the composition of triphenyl-rosaniline, $C^{20}H^{16}(C^6H^5)^3N^3$, and will be described as a derivative of rosaniline (p. 472).

**Aniline-brown.** A brown aniline dye, patented by G. De Laire (London Journal of Arts, Dec. 1863), is obtained by heating 1 pt. of fused aniline-blue with 4 pts. of anhydrous hydrochlorate of aniline to 240° for several hours. It is soluble in water, alcohol and acids, and is precipitated from the aqueous solution by salts.

The same dye is obtained by treating arsenate of aniline with the hydrochlorate (London Journal of Arts, Dec. 1863; Bull. Soc. Chim. [2] ii. 240).

**Aniline-green** or **Emeraldine.** Almost all the blue substances produced from aniline by the action of hypochlorous acid, and the other reagents above mentioned, become green when treated with acids, and blue again under the influence of alkalis. A very fine bright green is produced on cotton by printing with acid hydrochlorate of aniline on fabrics prepared with chlorate of potassium. This is called emeraldine. By subsequently passing the cloth through a solution of acid chromate of potassium, the colour is changed to the deep indigo-blue called azurine. (Calvert.)

**Aniline-purple** or **Mauve,** also called *Anileine, Indisine, Phenameine, Violine, Rosoline, Tyraline.* This is the dye discovered by Perkin and patented by him in 1856 (No. 1984, Aug. 26). To prepare it, a cold dilute solution of the sulphate (or any other salt) of commercial aniline is mixed with a solution, also cold and dilute, of acid chromate of potassium (bichromate of potash), the mixture being well stirred and left to itself for ten or twelve hours. A black precipitate is then produced which is collected on a filter, washed with cold water, dried, and digested with light coal-tar oil, which dissolves out a black tarry substance. The residue is again dried and digested with alcohol, wood-spirit, or any other liquid capable of dissolving the colouring matter; and the clear solution is separated by filtration or decantation, and distilled to recover the alcohol or wood-spirit. The residue then remaining is aniline-purple.

On the large scale this process has been variously modified by different manufacturers. Some complete the operation of mixing in a few minutes; others prolong it even to thirty-six hours. Many again find it convenient to employ the solution rather warm and concentrated, the temperature and degree of concentration depending also on the quantities employed. Hydrochlorate of aniline, obtained by dissolving aniline in commercial hydrochloric acid, is also frequently used. The sulphate is employed in a state of paste, as produced by treating aniline with oil of vitriol diluted with a very little water. The following proportions are recommended by Scheurer-Kestner: one kilogramme of aniline, a concentrated solution of from 800 to 1200 grammes of dichromate of potassium, and 500 grammes of sulphuric acid of sp. gr. 1·84 (60° Bm.).

The purification also is often differently conducted, more especially with the view of avoiding the use of expensive solvents. The black precipitate, after washing with cold water, is exhausted by prolonged ebullition with large quantities of water (sometimes acidulated with from 1 to 2 per cent. of acetic acid), whereby the colouring matter is dissolved. The filtered solutions are concentrated as much as possible, and while boiling are precipitated by caustic soda; the precipitate is washed on a filter with an alkaline solution, to remove the excess of potassic chromate together with a reddish colouring matter which affects the brilliancy of the purple, then treated with cold water till the alkali is removed and the washings have become coloured; and the precipitate is allowed to drain, whereby the aniline-purple is obtained in the form of paste. Very often the extraction by boiling water and precipitation by caustic soda are repeated in order to obtain the colour in a pure state. The solution of the paste in alcohol, wood-spirit or methylated spirit yields on evaporation a residue of a resinous appearance, exhibiting a peculiar metallic lustre, recalling at once that of gold and that of copper. It is soluble in water, more soluble in acetic acid, and the alcohols, and possesses extraordinary tinctorial powers.

Aniline-purple may also be obtained by the following processes: α. Oxidation of a cold dilute solution of hydrochlorate of aniline by a dilute solution of chloride of lime (Bolley, Beale and Kirkham). The aniline is thereby converted into a black pitch-like mass, the weight of which is not more than one-tenth of the quantity of aniline employed. This mass contains (*a*) aniline-purple; (*b*) a brown colouring matter soluble in alkaline liquids, and (*c*) a resinous substance soluble in alcohol, ether and sulphide of carbon. The aniline-purple is extracted by water; it is more difficult of purification than the compound prepared by Perkin's method. The chloride of lime process is more economical, but the colour of the product is less beautiful and of a redder tint than the preceding.—β. Oxidation of a salt of aniline in aqueous solution by peroxide of manganese, or by peroxide of lead (D. S. Price) under the influence of an acid.—γ. Oxidation of an aniline salt by a solution of potassic permanganate (Greville Williams), or of ferricyanide of potassium (R. Smith).—δ. Oxidation of a salt of aniline in aqueous solution by free chlorine or free hypochlorous acid (R. Smith), or by the double chloride of copper and sodium (Dale and Caro).* Of all these processes those only have attained industrial importance in which chromate of potassium, chlorate of potassium, chloride of lime, and chloride of copper are employed.

Aniline-purple prepared by Perkin's process is the sulphate of a base called Mauveine, having the composition $C^{27}H^{24}N^4$ (Perkin, Ann. Ch. Pharm. cxxxii. 201). On adding caustic potash to a solution of the commercial crystallised product, the colour changes immediately from purple to bluish-violet, and on standing, the mauveine separates as a crystalline body which, after washing with alcohol and then with water, appears as a nearly black glistening substance not unlike specular iron ore. It dissolves in *alcohol*, forming a violet solution, which on addition of acids immediately assumes a purple colour. It is insoluble or nearly so in ether and in benzene. It is a very stable compound and decomposes ammonium-salts with facility. When strongly heated, it decomposes, giving off a basic oil, which does not appear to be aniline.

*Acetate of Mauveine* is obtained by dissolving the base in boiling alcohol and acetic acid; it crystallises as the liquid cools, and may be purified by recrystallising it once or twice. It is a beautiful compound having a green metallic lustre.

*Carbonate of Mauveine*, $C^{27}H^{24}N^4.H^2CO^3$.—Solutions of mauveine quickly absorb carbonic acid from the air, the colour changing from violet to purple. To prepare the carbonate, carbonic acid gas is passed through boiling alcohol containing mauveine in suspension; on leaving the liquid to itself, the carbonate separates in prisms having a green metallic reflex. On boiling its solution, part of the carbonic acid escapes, the liquid at the same time assuming the violet colour of the free base. In the dry state the salt decomposes very quickly, and at 100° it gives off the whole of its carbonic acid and acquires a dark olive-brown colour. By analysis it was found to contain 8·8 per cent. $CO^2$, which is intermediate between the composition of a neutral carbonate $2C^{27}H^{24}N^4.H^2CO^3$, requiring 5·1 percent., and that of an acid carbonate $C^{27}H^{24}N^4.H^2CO^3$, requiring 9·1 per cent. $CO^2$.

*Hydriodate of Mauveine*, $C^{27}H^{24}N^4.HI$, crystallises in prisms having a green metallic lustre; less soluble than the following salt. In preparing it from the free base it is necessary to use colourless hydriodic acid, as free iodine would decompose it.

*Hydrobromate of Mauveine*, $C^{27}H^{24}N^4.HBr$.—Prepared like the hydrochlorate, which it resembles, excepting that it is less soluble.

*Hydrochlorate of Mauveine*, $C^{27}H^{24}N^4.HCl$, is obtained by direct combination of the acid and base, and separates from an alcoholic solution prepared at the boiling heat in small prisms, often grouped in tufts and having a strong green metallic lustre. It is moderately soluble in alcohol, less soluble in water, and nearly insoluble in ether. The *chloro-aurate*, $C^{27}H^{24}N^4.HCl.AuCl^3$, prepared by mixing the alcoholic solutions of the hydrochlorate and auric chloride, separates as a crystalline precipitate which is much less lustrous than the platinum-salt, and appears to lose a portion of its gold when recrystallised.

The *chloroplatinate*, $2(C^{27}H^{24}N^4.HCl).PtCl^4$, prepared like the gold-salt, separates from cold solutions as a green crystalline powder; from moderately warm solutions in rather large crystals. It possesses the green lustre of the hydrochlorate, but when dry has more of a gold colour. It is very slightly soluble in alcohol.

*Sulphate of Mauveine*, $2C^{27}H^{24}N^4.SH^2O^4$.—This salt is the original aniline-purple obtained by treating aniline with acid chromate of potassium and sulphuric acid.

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[*] For the dates of the Specifications of these and other patented processes for the preparation of aniline colours see *Hofmann's Report*.

Respecting the methods of dyeing with aniline-purple, see DYEING (ii. 357); also, *Hofmann's Report*, p. 124.

**Aniline Red** or **Rosaniline:** also called *Roseine, Fuchsine, Azaleine, Magenta, Solferino*, &c.—It has been known for some years that aniline, when subjected to the action of various reagents, is capable of yielding products of a deep red colour. The production of this red colour by the action of strong nitric acid on aniline was observed by Hofmann in 1843, and about the same time by Zinin. Hofmann also found that a dark red liquid is produced on mixing sulphate of aniline with ferric sulphate; and Natanson in 1856 observed a red substance among the products of the action of Dutch liquid upon aniline. But it was only in 1858 that the formation of a crimson colouring principle and some of its characteristic properties were first definitely pointed out by Hofmann, who, in studying the action of tetrachloride of carbon upon aniline, observed and described the formation of a basic substance which, when dissolved in alcohol, imparts to this liquid a magnificent crimson colour (see p. 465).[*] Since that time aniline-reds have been produced by treating aniline with a great variety of reagents, the most important of which are tetrachloride of tin, arsenic acid, nitric acid, mercuric nitrate and ferric chloride. Patents have also been taken out for the preparation of these colours by the ebullition of aniline with stannous, mercurous and mercuric sulphates; with ferric, uranic, argentic and plumbic nitrates; with stannic and mercuric bromides; with iodine, stannic iodide and iodoform; with mercuric chlorate, bromate and iodate; and with pentachloride of antimony; also by the action of antimonic oxide, peroxide of bismuth, stannic, ferric, mercuric and cupric oxides on hydrochlorate or sulphate of aniline at the temperature of 180°. The greater number of these processes, however, are of but little value; we proceed to describe those which are actually practised on the manufacturing scale.

1. *Preparation of Aniline-red by Tetrachloride of Tin.*—This process, discovered by Messrs. Vergnin and Renard, of Lyons, was the first by which aniline-red was prepared for industrial use. A mixture of 10 pts. aniline and 6 to 7 pts. tetrachloride of tin, either anhydrous or hydrated, is heated to ebullition for fifteen or twenty minutes, the liquid becoming at first yellow, then red, and being ultimately converted into a nearly black mass. The mixture is left to cool and then treated with a large quantity of boiling water, which acquires a magnificent red colour, and without any further preparation, forms a splendid dye-bath for silk and wool. It is found better, however, to precipitate the colouring matter by partially saturating the concentrated liquid with carbonate of sodium, and adding common salt. The aniline-red is then precipitated in the solid state, and has only to be dissolved in water, alcohol, or acetic acid to prepare a dye-bath for imbuing silk and wool with the most beautiful roseate tints.

Anhydrous mercuric, ferric or cupric chloride may be used in the preparation instead of the stannic chloride.

2. *Preparation of Aniline-red with Arsenic Acid.*—This process, which is one of the best, was discovered by Medlock. It consists in combining arsenic acid with a slight excess of aniline, and heating the crystalline mass over a slow fire to about 120—140°, care being taken not to exceed 160°. The proportions recommended are 12 pts. of the dry acid of commerce (which is chiefly a dihydrate containing 13·5 per cent. water) to 10 pts. of aniline, with or without the addition of water. The operation, according to the scale on which it is carried out, requires from four to nine hours for completion. A perfectly homogeneous fluid mass is thus obtained, which on cooling solidifies to a hard substance with metallic bronze-coloured lustre. When dissolved in boiling water it produces a solution of great richness and purity of colour. From this solution the colouring matter may be precipitated almost free from arsenic by addition of a slight excess of soda. The precipitate is collected on filters, washed with a little cold water, and redissolved in acetic acid.

3. With *Mercuric Nitrate.* (Gerber-Keller's process.)—7 or 8 pts. of pulverised mercuric nitrate are gradually added, with constant stirring, to 10 pts. of aniline heated in a water-bath (too high a temperature might cause a violent and explosive reaction). The operation lasts eight or nine hours, at the end of which time the mass becomes of a magnificent violet-red colour. This constitutes the azaleine of commerce. The mercury is reduced during the process to the metallic state, and may be used again for the preparation of the nitrate.

4. With *Nitric Acid.* (Lauth and Depouilly's process.)—This process ought more properly to be called treatment of nitrate of aniline with aniline, as it requires the aniline to be in excess. The mixture is heated to about 150° or 160°, care being taken to remove the heat as soon as the reaction becomes at all lively. After several hours a mass is obtained of a fine violet-red colour, which may be sent into commerce as soon

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[*] This mode of producing aniline-red has not actually been carried out in practice; but a Committee of the *Société industrielle de Mulhouse* have reported favourably on the possibility of performing it economically on the manufacturing scale.

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as it has been treated with a small quantity of carbonate of sodium dissolved in water, and precipitated by addition of common salt. This process gives good results especially on the small scale; but when large quantities are operated on, it is often difficult to regulate the action, and combustion and deflagration ensue, which of course destroy the entire product.

The aniline-red obtained by the action of nitric acid or mercuric nitrate has a more violet tint than that prepared by means of the anhydrous chlorides.

5. *Direct production of Aniline-red from Nitrobenzene.*—Nitrobenzene is treated with a mixture of iron and hydrochloric acid, or with ferrous chloride, whereby it is converted into aniline, with formation of ferric chloride (p. 420). On heating the mixture, the ferric chloride reacts upon the aniline thus produced, converting it into aniline-red. Messrs. Laurent and Casthélaz, to whom this process is due, give the name of *erythrobenzol* to the colouring matter thus obtained; but it probably consists mainly of rosaniline.

*Purification of Aniline-red.*—The crude colours obtained by the preceding processes still contain undecomposed aniline, chiefly in the form of salts, together with tarry matters, some insoluble in water and dilute acids, others soluble in sulphide of carbon, naphtha, or in caustic or carbonated alkalis. On boiling the crude red with excess of alkali, the undecomposed aniline is expelled, the acid which exists in the product being fixed by the alkali, while very little of the colouring matter dissolves. On treating the slightly washed residue with boiling water acidulated with a mineral acid, the red is dissolved, while certain tarry matters remain insoluble; and if the boiling solution be filtered and saturated with an alkali, the colouring matter is precipitated tolerably pure. The precipitation may be hastened by dissolving common salt in the saturated solution. By once more redissolving the precipitated red in an acid, not employed in excess, a solution is obtained which frequently crystallises, or from which the pure red may be thrown down by a new addition of chloride of sodium or other alkaline salt.

In France the hydrochlorate, in England the acetate, of aniline-red is generally used in dyeing.

*Composition and Formation of Aniline-red.*—Hofmann has shown that all the varieties of aniline-red are salts of an organic base which he designates as **rosaniline**. This base is a triamine, $C^{20}H^{19}N^3$, capable of uniting with one or three (probably also with two) atoms of acid. Moreover three of its hydrogen-atoms may be replaced by alcohol-radicles, namely methyl, ethyl, amyl, phenyl, and tolyl or benzyl, producing blue and violet dyes. Further than this, its rational constitution has not been distinctly made out. Neither is its mode of formation thoroughly understood; but one very important fact has been brought to light by the researches of Hofmann, and confirmed by the experience of manufacturers, namely that pure aniline, from whatever source it may be obtained, is incapable of furnishing aniline-red. Commercial aniline prepared from coal-tar always in fact contains toluidine (benzylamine, $C^7H^9N$) as well as phenylamine; and Hofmann has shown that the presence of this base together with aniline is essential to the formation of the red dye. Toluidine by itself is just as incapable of yielding the red as pure aniline, but when a mixture of pure aniline and pure toluidine is treated with stannic or mercuric chloride, or with arsenic acid, the red colouring matter is immediately produced. Its formation may perhaps be represented by the equation:

$$\underset{\text{Aniline.}}{C^6H^7N} \quad + \quad \underset{\text{Toluidine.}}{2C^7H^9N} \quad = \quad \underset{\text{Rosaniline.}}{C^{20}H^{19}N^3} \quad + \quad H^6,$$

and its constitution by the formula $\left.\begin{matrix}(C^7H^6)^2\\(C^6H^4)''\\H^3\end{matrix}\right\}N^3$, containing the diatomic radicles phenylene and tolylene or benzylene. (**Hofmann**, Proc. Roy. Soc. 485.)

**Schiff** (Ann. Ch. Pharm. cxxv. 360; cxxvii. 337) has endeavoured to show that the formation of aniline-red depends upon the previous formation of certain compounds of aniline with metallic salts, and the subsequent decomposition of these compounds, and he gives a general equation by which he supposes this decomposition to be represented; but this theory is manifestly erroneous, inasmuch as it takes no cognisance of the essential fact that the formation of the red dye depends upon the presence of toluidine as well as of aniline.

**Rosaniline** when separated from the solution of its salts by precipitation with an alkali exhibits the composition,

$$C^{20}H^{21}N^3O \quad = \quad C^{20}H^{19}N^3.H^2O.$$

On mixing the boiling solution of the acetate with a large excess of ammonia, a rose-red somewhat crystalline precipitate is formed, consisting of the hydrate in a tolerably pure state; and the colourless liquid filtered from this precipitate while boiling, deposits on cooling white needles and plates of the perfectly pure hydrate.

Rosaniline is nearly insoluble in *water*, slightly soluble in *ammonia*, more soluble in *alcohol*, with deep red colour, insoluble in *ether*. When exposed to the air, it rapidly becomes rose-coloured and ultimately of a deep red, probably in consequence of the formation of a carbonate.

Rosaniline is a rather powerful base, forming, as already observed, mono-acid and triacid salts, almost all of which are remarkable for their beauty and the facility with which they crystallise. They may be prepared either by direct union of the acid with the free base, or by boiling the ammonium-salts of the several acids with excess of the base.

The *mono-acid salts* exhibit for the most part by reflected light, the lustrous metallic green of the wings of the rose-beetle; in transmitted light the crystals are red, becoming opaque when they acquire certain dimensions. The solutions of these salts in water or alcohol possess the magnificent crimson colour which characterises rosaniline compounds. According to Chevreul (Compt. rend. liii. 984) the green colour reflected from the crystals of these salts is exactly complementary to the crimson colour which the solutions impart to wool and silk. The *tri-acid salts* of rosaniline are yellowish-brown, both in the solid state and in solution. They are much more soluble in water and alcohol than the mono-acid salts.

The salts of rosaniline when treated with reducing agents, sulphide of ammonium for example, are converted into leucaniline (iii. 574):

$$\underset{\text{Rosaniline.}}{C^{20}H^{19}N^3} \quad + \quad H^2 \quad = \quad \underset{\text{Leucaniline.}}{C^{20}H^{21}N^3.}$$

*Acetate of Rosaniline*, $C^{20}H^{19}N^3.C^2H^4O^2$.—This is perhaps the finest of all the rosaniline-salts, sometimes separating from large quantities of solution in crystals an inch in diameter. It is very soluble in water and alcohol, and does not crystallise well from small quantities of solution. The crystals when freshly prepared exhibit in a high degree the green metallic lustre already mentioned, but on protracted exposure to light, this colour disappears, the crystals assuming a dark reddish-brown tint.

*Hydrochlorates.*—The mono-acid salt, $C^{20}H^{19}N^3.HCl$, is deposited from its boiling solution in well-defined rhombic plates, frequently in stellar forms. It is but sparingly soluble in water, more soluble in alcohol, insoluble in ether. It retains a small quantity of water at 100°, but becomes anhydrous at 130°. Like most rosaniline-salts, it is very hygroscopic. Treated with zinc and hydrochloric acid, it yields leucaniline.

The tri-acid hydrochlorate, $C^{20}H^{19}N^3.3HCl$, is obtained by adding very strong hydrochloric acid to a warm solution of the base in moderately strong acid. The whole then solidifies on cooling to a network of beautiful brown needles, which must be washed with strong hydrochloric acid and dried in a vacuum over lime and oil of vitriol, as water decomposes them, reproducing the mono-acid salt. The tri-acid salt gives off part of its acid at 100°, the brown crystals becoming indigo-blue, and being ultimately converted into the green crystals of the mono-acid salt.

Both the hydrochlorates of rosaniline unite with tetrachloride of platinum, forming uncrystallisable double salts which appear to contain $2(C^{20}H^{19}N^3.HCl).PtCl^4$ and $2(C^{20}H^{19}N^3.3HCl).3PtCl^4$ respectively.

*Hydrobromate of Rosaniline*, $C^{20}H^{19}N^3.HBr$, resembles the mono-acid hydrochlorate in every respect, but is even less soluble. The *hydriodate*, $C^{20}H^{19}N^3.HI$, forms green very soluble needles.

*Nitrate of Rosaniline*, $C^{20}H^{19}N^3.NHO^3$, obtained by dissolving the base in warm dilute nitric acid, forms small crystals resembling the other salts of rosaniline.

The *picrate* or *trinitrophenate*, $C^{20}H^{19}N^3.C^6H^2(NO^2)^3O$, crystallises in beautiful reddish needles, likewise very sparingly soluble in water.

*Sulphates.*—The neutral salt, $(C^{20}H^{19}N^3)^2H^2SO^4$ (at 130°), obtained by dissolving the base in dilute sulphuric acid, is deposited in green crystals having a metallic lustre.

*Tannates.*—Tannic acid added to an aqueous solution of rosaniline, either neutral or acid, throws down the whole of the rosaniline in the form of an insoluble tannate. The precipitate formed in cold dilute solutions has an intense carmine colour, like the carmine-lake of cochineal; from warm concentrated solutions it separates as a tenacious, pitchy, red-brown mass. If the tannic acid is in excess, the solution retains a red colour, indicating the formation of a more soluble (di- or tri-acid) salt. The neutral tannate is likewise formed when cloth mordanted or printed with tannic acid is dipped in a slightly acid solution of aniline-red. It dissolves in alcohol, wood-spirit and acetic acid with the deepest crimson colour; in concentrated solutions of the stronger acids with reddish-yellow colour, which however changes to red on addition of water, part of the salt being at the same time precipitated; by prolonged boiling with concentrated acids it is decomposed. Alkalis decolorise it, but the colour is restored by neutralisation with an acid. When tannate of rosaniline is triturated with three or four times its weight of wood-spirit and the thickish carmine-coloured mass is mixed with a quantity

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of nitric or hydrochloric acid (or better with alcohol saturated with hydrochloric acid), equal to $\frac{1}{20}$ to $\frac{1}{10}$ of the volume of the wood-spirit, the colour of the mixture—which dries up quickly if the trituration be continued—passes into violet and finally into blue. By duly regulating the proportion of acid, any required shade of colour may be obtained. As these blue and violet colouring matters are nearly insoluble in water, they may be freed from adhering acid by washing with water. For dyeing, they are dissolved in alcohol or wood-spirit, and the solution is diluted with water. (E. Kopp, Jahresb. 1862, p. 694.)

*Dyeing with Aniline-red.*—The salts of rosaniline chiefly employed for dyeing silk and wool are the acetate, hydrochlorate and nitrate; their application is very simple. Silk is dyed by passing it through a cold aqueous solution of the salt; for the dyeing of wool the solution is heated to 50° or 60° C. Rosaniline is precipitated from its solutions and fixed by silk and wool, with such rapidity and force that it is necessary to operate with solutions comparatively weak at first and only gradually strengthened; otherwise the dye will be unequal, the portions first immersed being more strongly coloured than the rest. Cotton, on the other hand, has no attraction for this colouring matter, and requires first to be treated with some animal mordant, such as albumin, prepared glutin, casein, lactarin or gelatin, or with tannic acid, the latter being used either in its combinations with metallic oxides, as antimonic, stannic or plumbic, or as tannate of gelatin. For some time, oily preparations were employed, such as sulphomargaric or sulpholeic acid.

When a stuff which has been dyed with aniline-red is printed with a strong acid, it it decolorised, with formation of a yellowish stain in consequence of the conversion of the mono-acid salt of rosaniline into a tri-acid salt, which has but little colour; but on washing the material with water, the excess of acid is removed and the red colour is restored. On printing with a powerful base, caustic soda for example, the red rosaniline salt is decomposed and colourless rosaniline is liberated, but when the soda is washed out with water, the red colour reappears, the rosaniline probably becoming carbonated. Ammonia likewise destroys the colour for a time, but as the ammonia escapes the red-coloration returns. If however the dyed fabric be left for some time in contact with weak aqueous ammonia, the rosaniline is for the most part dissolved out, and the colour is then no longer restored by rinsing with water.

### *Derivatives of Rosaniline.*

**Triethyl-rosaniline,** $C^{26}H^{31}N^3 = C^{20}H^{16}(C^2H^5)^3N^3$.—This compound, which yields one of the varieties of aniline-violet, was discovered by Hofmann (Proc. Roy. Soc. xiii. 13; Bull. Soc. Chim. 1865, [1] 155), and is known in commerce as *Hofmann's violet.* It is obtained by heating 1 pt. of rosaniline, 2 pts. iodide of ethyl, and about 2 pts. of strong alcohol to 100° for three or four hours, in a vessel capable of resisting a certain amount of pressure. The mixture is then left to cool, and the syrupy violet mass is dissolved in alcohol or wood spirit. The resulting solution of hydriodate of triethyl-rosaniline may be used for dyeing and printing just like the other aniline dyes. By using them in this manner, however, the iodine, which is a substance of some value, is lost. It may be recovered by boiling the product, either before or after solution in alcohol, with a caustic alkali, which precipitates the triethyl-rosaniline, leaving the alkaline iodide in solution. From this solution the iodine may be recovered in the usual way, and employed for the preparation of a fresh quantity of ethylic iodide. The triethyl-rosaniline is washed with water till all the soluble salts are removed, then dissolved in alcohol, containing hydrochloric acid, or in acetic acid more or less diluted with water, and this solution is used for dyeing and printing.

If the triethyl-rosaniline obtained as above be again treated with iodide of ethyl, and the series of operations repeated two or three times, the ultimate product is an *ethyliodate of triethyl-rosaniline*, $C^{26}H^{31}N^3.C^2H^5I$.

Similar products are obtained by treating rosaniline with the iodide of methyl at 100° or iodide of amyl at 150°—160°.

*Other varieties of Aniline-violet.*—By heating a salt of rosaniline with a quantity of aniline less than sufficient to form aniline-blue, *e.g.* equal parts of hydrochlorate of rosaniline and aniline to 180°, a violet colouring matter is produced, which was originally patented by MM. Girard and De Laire, and is known in commerce as *violet impérial.* It is likewise obtained together with aniline-blue, when a salt of rosaniline is heated with excess of aniline (p. 472). Its composition has not been ascertained, but it is perhaps a mixture of rosaniline and triphenyl-rosaniline, or a mono- or diphenylic rosaniline.

Another aniline-violet has been obtained by Nicholson. It is formed by carefully heating aniline-red to a temperature between 200° and 215°. Ammonia is then given off, and a dark semi-solid mass is formed. This is exhausted with acetic acid, and the deep violet solution diluted with sufficient alcohol to give the dye a convenient strength for commercial purposes.

Lastly, Perkin's mauveine must be regarded as a variety of aniline-violet; but as its salts have a purple colour, it is best to designate this colouring matter as aniline-purple, the name originally given to it by its discoverer.

**Triphenyl-rosaniline,** $C^{38}H^{31}N^3 = C^{20}H^{16}(C^6H^5)^3N^3$.—This base, the salts of which form the spendid blue dye called aniline-blue, also "Bleu de Paris," or "Bleu de Lyon," was discovered by Girard and De Laire, and its constitution has been determined by Hofmann (Proc. Roy. Soc. xiii. 9). It is produced by heating a salt of rosaniline, or a mixture of substances capable of producing such a salt, with excess of aniline: *e. g.*

$$\underset{\text{Hydrochlorate of Rosaniline.}}{C^{20}H^{19}N^3.HCl} + \underset{\text{Aniline.}}{3(C^6H^5.H^2.N)} = \underset{\text{Hydrochlorate of Triphenyl-rosaniline.}}{C^{20}H^{16}(C^6H^5)^3N^3.HCl} + 3NH^3.$$

The time required varies with the quantity of material operated upon. If a mixture of 2 kilogrammes of hydrochlorate of rosaniline and 4 kilogrammes of aniline be employed, the operation is complete in four hours.

Several other colouring matters are however formed at the same time, among which are a violet (*violet impérial*) and a green; large quantities of ammonia are also given off. The crude blue is purified by treating it successively with boiling water acidulated with hydrochloric acid, and afterwards with pure water.

Triphenyl-rosaniline is obtained on pouring a concentrated solution of the hydrochlorate in ammoniacal alcohol into water, as a white or greyish precipitate consisting of a hydrate, $C^{38}H^{31}N^3.H^2O$. It shows a tendency to crystallise, but has not hitherto been obtained in distinct crystals. The alcoholic and ethereal solutions deposit it in the amorphous state, even on spontaneous evaporation. It is very liable to change, gradually becoming blue during washing, and especially during drying, even in vacuo. The vacuum-dry substance heated to 100°, assumes a deep brown colour which it retains on cooling; it likewise undergoes slight fusion also at that temperature, but does not lose weight.

The salts of triphenyl-rosaniline are prepared by treating the free base with acids Only mono-acid salts have hitherto been obtained. The solutions treated with zinc and hydrochloric acid, or other reducing agents, are rapidly decolorised and converted into salts of triphenyl-leucaniline, $C^{38}H^{33}N^3$ (iii. 574).

*Hydrochlorate of Triphenyl-rosaniline*, $C^{38}H^{31}N^3.HCl$, is the aniline-blue obtained by the process above described. It is an indistinctly crystalline powder of a bluish-brown colour becoming pure brown at 100°. It is perfectly insoluble in water whether cold or boiling, insoluble also in ether, but dissolves, though with difficulty, in alcohol, forming a solution of a splendid deep blue colour.

From the boiling saturated alcoholic solution it is deposited on cooling in the form of imperfect crystalline granules. The same solution when evaporated leaves it as a thin film, which reflects light with a peculiar metallic, half-golden, half-coppery lustre (Hofmann). It dissolves in strong sulphuric acid, and on digesting the solution for half an hour at 150° and then adding water, the blue colouring matter is precipitated in a modified state, having in fact become soluble in pure water. (Nicholson.)

The *hydrobromate, hydriodate, nitrate* and *sulphate*, $(C^{38}H^{31}N^3)^2H^2SO^4$, have also been prepared. They resemble the hydrochlorate, but the nitrate is perhaps a little more, the sulphate a little less, soluble in alcohol.

*Various processes for the production of Aniline-blue.*—Rosaniline-salts assume a permanent blue coloration when boiled with solutions of aldehydes (Lauth, Quesneville's Monit. Scient. [1863] iv. 238); or with crude wood-spirit (E. Kopp, *ibid.* p. 332).

Tannate of rosaniline appears to be especially inclined to this change. The nature of the blue colouring matter thus produced is unknown, but it is probably identical with that produced by treating rosaniline with excess of aniline. The same remark applies to a blue dye described by Gros-Renaud and Schäffer of Mulhouse (*ibid.* iii. 292) under the name of *Mulhouse blue*, which is formed by boiling the solution of a rosaniline salt (generally the nitrate) with a solution of gum-lac and carbonate of sodium.

**Tritolyl-rosaniline** or **Toluidine-blue,** $C^{41}H^{37}N^3 = C^{20}H^{16}(C^7H^7)^3N^3$ (Hofmann, Ann. Ch. Pharm. cxxxii. 290).—Produced by heating the acetate (or other salt) of rosaniline with twice its weight of toluidine (benzylamine). The reaction is precisely similar to that by which triphenyl-rosaniline is obtained:

$$C^{20}H^{19}N^3 + 3C^7H^9N = C^{41}H^{37}N^3 + 3NH^3.$$

Large quantities of ammonia are evolved, and a brown metallic-shining mass is obtained which dissolves in alcohol with deep indigo colour. This product is acetate of tritolyl-rosaniline. When treated with alcoholic ammonia, and subsequently with water, it yields the base from which various salts may be prepared. These salts resemble those of triphenyl-rosaniline; but they are more soluble and more difficult to crystallise. The *hydrochlorate* crystallises from boiling alcohol in small blue crystals insoluble in boiling water, and having when dried at 100° the composition $C^{41}H^{37}N^3.HCl$.

The salts of tritolyl-rosaniline when subjected to dry distillation, undergo a decomposition similar to that of the salts of triphenyl-rosaniline, yielding phenyl-tolylamine $(C^6H^5)(C^7H^7)HN$ (p. 454).

*Tolyl-diphenyl-rosanilin*, $C^{20}H^{16}(C^6H^5)^2(C^7H^7)N^3$, appears to be obtained as a hydrate by heating phenyl-tolylamine with mercuric chloride.

**Aniline-yellow** or **Chrysaniline,** $C^{20}H^{17}N^3$.—This colouring matter, which differs from rosaniline by containing 2 atoms of hydrogen less, is obtained as a bye-product in the preparation of aniline-red. When the residue from which the rosaniline has been extracted is submitted for some time to a current of steam, a quantity of chrysaniline passes into solution, and is precipitated in the form of a difficultly soluble nitrate on adding nitric acid to this solution. (Nicholson.)

Chrysaniline in the free state is an amorphous yellow powder, like recently precipitated chromate of lead, nearly insoluble in *water*, but dissolving readily in *alcohol* and in *ether*. It forms two series of crystallisable salts, mono-acid and di-acid.

The *di-acid hydrochlorate*, $C^{20}H^{17}N^3.2HCl$, is formed as a scaly precipitate on adding concentrated hydrochloric acid to a solution of the base in the dilute acid. It dissolves easily in water, less easily in alcohol, and not at all in ether. It forms a hydrate containing 1 atom of water. It does not lose weight between 100° and 120°, but when heated for a fortnight to 160°—180° it is converted into a yellow crystalline powder of the neutral salt $C^{20}H^{17}N^3.HCl$. which is somewhat less soluble in water than the acid salt. It unites with tetrachloride of platinum, forming a *chloroplatinate* which crystallises from a dilute solution in large beautiful tablets.

The *nitrates* of chrysaniline crystallise with the greatest facility in ruby-red needles which are so sparingly soluble in water that a solution of nitrate of potassium containing only 1 grm. of nitric acid in a litre, immediately yields a crystalline precipitate on addition of a chrysaniline-salt. The neutral nitrate, $C^{20}H^{17}N^3.NHO^3$, is obtained by boiling chrysaniline in excess with dilute nitric acid; and the solution of this salt mixed with cold concentrated nitric acid, yields the acid nitrate, $C^{20}H^{17}N^3.2NHO^3$, in crystals resembling ferricyanide of potassium and decomposible by water.

*Sulphate of chrysaniline* is easily soluble and difficult to crystallise. (Hofmann.)

Chrysaniline and its salts dye silk and wool a splendid golden-yellow colour.

Schiff (Ann. Ch. Pharm. cxxvii. 342), by triturating aniline with 2 pts. of potassic antimonate or stannate, and supersaturating with hydrochloric acid, obtained a scarlet colouring matter soluble in ether-alcohol, and forming with hydrochloric acid a salt which crystallised from ether in laminæ resembling cantharides, and yielded with alkalis a deep yellow flocculent body capable of imparting a permanent yellow dye to silk and wool.

**PHENYLAMMONIUMS.** Compounds derivable from ammonium, $NH^4$, by the substitution of phenyl or derivatives of phenyl, &c., for equivalent quantities of hydrogen.

### 1. *Phenylammoniums containing only Alcohol-radicles.*

All the salts of aniline and its derivatives described in the preceding pages may be regarded either as compounds of ammonia-molecules with acids, or of ammonium-molecules with salt-radicles: *e. g.*

$$\underset{\substack{\text{Hydrochlorate of}\\\text{phenylamine.}}}{(C^6H^5)H^2N.HCl} \quad = \quad \underset{\substack{\text{Chloride of phenyl-}\\\text{ammonium.}}}{(C^6H^5)H^3N.Cl}$$

$$\underset{\substack{\text{Nitrate of diethyl-phenyl-}\\\text{amine.}}}{(C^6H^5)(C^2H^5)^2N.HNO^3} \quad = \quad \underset{\substack{\text{Nitrate of diethyl-phenyl-}\\\text{ammonium.}}}{(C^6H^5)(C^2H^5)^2HN.NO^3}$$

$$\underset{\substack{\text{Sulphate of chloro-}\\\text{phenylamine.}}}{(C^6H^6ClN)^2.H^2SO^4} \quad = \quad \underset{\substack{\text{Sulphate of chloro-}\\\text{phenylammonium.}}}{(C^6H^7ClN)^2SO^4}$$

But there are certain compounds which cannot be formulated as compounds of phenylamines with acids, but must be regarded either as phenylamines combined with compound ethers (alcoholic sulphates, iodides, &c.), or else as salts of phenylammoniums: *e.g.*

$$\underset{\substack{\text{Methyl-iodate of ethyl-amylo-}\\\text{phenylamine.}}}{(C^6H^5)(C^5H^{11})(C^2H^5)N.CH^3I} \quad = \quad \underset{\substack{\text{Iodide of methyl-ethyl amylo-}\\\text{phenylammonium.}}}{(C^6H^5)(C^5H^{11})(C^2H^5)(CH^3)N.I}$$

The latter view affords the best explanation of most of their reactions.

The iodides of these phenylammoniums in which the whole of the hydrogen is replaced by alcohol-radicles, are obtained by heating a tertiary phenylamine with an alcoholic iodide in sealed tubes; thus diethylaniline $(C^6H^5)(C^2H^5)^2N$, heated with iodide of ethyl, yields iodide of triethylo-phenylammonium. The iodides thus obtained when treated with moist oxide of silver, yield the corresponding hydrates, which are strong alkaline bases like hydrate of tetrethylammonium (ii. 561), and cannot be distilled without decomposition; the hydrate treated with acids, yields various salts.

*Triethylphenylammonium*, $C^{12}H^{20}N = (C^6H^5)(C^2H^5)^3N$. (**Hofmann**, Ann. Ch. Pharm. lxxix. ii.)—The *hydrate*, $C^{12}H^{20}N.H.O$, forms a bitter alkaline solution which when evaporated and distilled is resolved into water, ethylene, and diethylaniline:

$$\left.\begin{matrix}(C^6H^5)(C^2H^5)^3N\\H\end{matrix}\right\}O \quad = \quad H^2O \;+\; C^2H^4 \;+\; (C^6H^5)(C^2H^5)^2N.$$

The *chloride*, $C^{12}H^{20}NCl$, crystallises with moderate facility. The *chloroplatinate*, $2C^{12}H^{20}NCl.PtCl^4$, is a light-yellow amorphous precipitate very slightly soluble in water, insoluble in alcohol and ether.

The *iodide* is a crystalline mass obtained by heating a mixture of diethylaniline and iodide of ethyl in a sealed tube for two hours at the heat of the water-bath, and removing the excess of ethylic iodide or diethylaniline by distillation.

The *sulphate*, *nitrate*, and *oxalate* crystallise readily.

*Methyl-ethyl-amylo-phenyl-ammonium*, $C^{14}H^{24}N = (C^6H^5)(CH^3)(C^2H^5)(C^5H^{11})N$.—The *hydrate* yields by distillation water, ethylene gas and methyl-amylaniline:

$$\left.\begin{matrix}(C^6H^5)(CH^3)(C^2H^5)(C^5H^{11})N\\H\end{matrix}\right\}O \;=\; H^2O + C^2H^4 + (C^6H^5)(CH^3)(C^5H^{11})N.$$

The *chloroplatinate*, $2C^{14}H^{24}NCl.PtCl^4$, is a light coloured non-crystalline precipitate. The *iodide* obtained by heating ethyl-amylaniline with methylic iodide is crystalline and soluble in water. (**Hofmann**, *loc. cit.*)

*Ethyl-triphenylammonium?* $= C^{20}H^{20}N = (C^6H^5)^3(C^2H^5)N$. (See p. 454.)

### 2. *Phenyl-ammoniums containing Metals.*

Aniline unites with several metallic salts, forming compounds which may be regarded as salts either of metallo-phenylamines or of metallo-phenylammoniums: thus with mercuric chloride it forms the compound $2C^6H^7N.Hg''Cl^2 = C^{12}H^{12}Hg''N^2.2HCl = C^{12}H^{14}Hg''N^2.Cl^2$. The general formula of these compounds is:

$$nC^6H^7N.M^{(n)}X^n \quad = \quad \left.\begin{matrix}M^{(n)}\\(C^6H^5)^n\\H^n\end{matrix}\right\}N^n.nHX \quad = \quad \left.\begin{matrix}M^{(n)}\\(C^6H^5)^n\\H^{2n}\end{matrix}\right\}N^n.X^n;$$

in which $M^{(n)}$ denotes an $n$-atomic metal, and X a monatomic salt-radicle such as Cl, $NO^3$, &c., $X^2$ being of course replaceable by $X^4$, $X^3$ by $X^{(6)}$, &c.*

ANTIMONY-COMPOUNDS. *Chloride of Triphenylstibonium*, $3C^6H^7N.SbCl^3 = \left.\begin{matrix}(C^6H^5)^3\\Sb'''\\H^3\end{matrix}\right\}N^3.Cl^3$, is obtained by heating aniline with dry antimonious chloride, or by adding aniline to a solution of the chloride in benzene, as a white crystalline mass, which is soluble only in aniline and separates therefrom in slender needles. It is decomposed by water, and is converted into a double salt by hydrochloric acid. It melts at 80°, solidifies again in long needles and is partially decomposed by distillation. (H. **Schiff**, J. pr. Chem. lxxxix. 226; Jahresb. 1863, p. 413.)

*Iodide of Triphenylstibonium*, &c., $Sb'''(C^6H^5)^3H^6N^3I^3$, is produced in like manner (at 100°—120°), and separates from the excess of aniline, in yellow needles which are decomposed by boiling with caustic alkalis, yielding aniline, antimonious oxide and iodide of potassium.

ARSENIC-COMPOUND. *Chloride of Triphenylarsonium*, $3C^6H^7N.AsCl^3 = As'''(C^6H^5)^3H^6N^3Cl^3$, obtained in like manner, is crystalline, melts at about 90°, and distils without decomposition between 205° and 210°. It is somewhat soluble in water, with separation of arsenious acid. The corresponding *iodide* is not altered either by cold water or by dilute sulphuric acid; but boiling alcohol decomposes it, yielding hydriodate of iodaniline, free aniline and brown flocks of proto-iodide of arsenic (**Schiff**, *loc. cit.*):

$$As(C^6H^5)^3H^6N^3I^3 \quad = \quad C^6H^6IN.HI \;+\; 2C^6H^7N \;+\; AsI.$$

BISMUTH-COMPOUNDS. *Chloride of Triphenyl-bismuthonium*, $3C^6H^7N.BiCl^3 =$

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* In the general formula given on page 428, $H^n$ is erroneously printed instead of $H^{2n}$; corresponding alterations are also required in the examples which follow on the same page.

$Bi'''(C^6H^5)^2H^6N^2Cl^3$, is a fusible, indistinctly crystalline mass which is very slowly decomposed by water, and turns violet when heated.

Aniline mixed with aqueous chloride of bismuth forms a precipitate consisting of $C^6H^7N.BiClO$. (Schiff.)

CADMIUM-COMPOUNDS. Resemble the zinc-compounds (*infra*).

COPPER-COMPOUND. *Sulphate of Phenyl-cuprammonium*, $2C^6H^7N.Cu''SO^4 = Cu''(C^6H^5)^2H^4N^2.SO^4$, is obtained as a green crystalline precipitate on adding cupric sulphate to a solution of aniline. Boiling water decomposes it, sulphate of aniline dissolving and a basic sulphate of copper being deposited (Gerhardt). Aniline forms with cupric chloride a similar precipitate which soon turns black (Hofmann).

MERCURY-COMPOUNDS. *Chloride of Diphenylmercurammonium*, $2C^6H^7N.Hg''Cl^2 = Hg''(C^6H^5)^2H^4N^2Cl^2$, sometimes called *chloromercurate of aniline*, is precipitated on adding mercuric chloride to an excess of alcoholic aniline. It is a nacreous precipitate which must be collected on a filter and washed with a small quantity of alcohol. It gives off a small quantity of aniline even at 60°, and turns yellowish (Gerhardt, *Traité*, iii. 86). According to Schiff, it decomposes at 100°, yielding aniline-red, and a similar red product is obtained by heating aniline with mercurous chloride to 150°. [Probably the aniline used contained toluidine (see p. 469).]

Another mercury-salt containing $C^{12}H^{14}Hg''N^2Cl^2.2Hg''Cl^2$ or $2C^6H^7N.3Hg''Cl^2$, rises to the surface as a pasty mass when aniline is mixed with [excess of?] aqueous corrosive sublimate; on mixing the alcoholic solutions, it is precipitated in the form of a soft white powder, which soon becomes crystalline. It must be washed with water. When boiled with water, it turns lemon-yellow, with evolution of a small quantity of aniline, and partial solution of the salt, which crystallises out without alteration on cooling. In a small quantity of hot hydrochloric acid it dissolves partially and melts into a heavy red oil; in a large quantity completely, and yields white crystals on cooling. In cold water it dissolves very sparingly; slightly also in boiling alcohol, from which it crystallises on cooling (Hofmann). Of the same composition also are probably the needles which Gerhardt obtained by further addition of corrosive sublimate to the alcoholic liquid filtered from the preceding salt, and which, when boiled with alcohol, yielded an orange-yellow residue and a dark yellow filtrate, from which a mixture of colourless and orange-yellow crystals were deposited on cooling.

*Cyanide of Diphenylmercurammonium*, $2C^6H^7N.Hg''Cy^2 = Hg''(C^6H^5)^2H^4N^2.Cy^2$, separates in long needles on mixing aniline with a hot aqueous solution of mercuric cyanide. It melts very easily, and is easily resolved into aniline and cyanide of mercury at 80°. It is not decomposed by alkalis. (Schiff.)

The corresponding *iodide* is obtained by double decomposition, in yellowish laminæ, and is converted into a red colouring matter at 100°. (Schiff.)

The *nitrate*, $Hg''(C^6H^5)^2H^4N^2.2NO^3$, is formed on mixing aniline or nitrate of aniline with mercuric nitrate, as a white precipitate which becomes crystalline in contact with dilute acids. When heated with water, it gives up nitrate of aniline, and is converted into white pulverulent nitrate of *diphenyl-dimercurammonium*, $\overset{\prime\prime}{Hg}{}^2(C^6H^5)^2H^2N^2.2NO^3.H^2O$, and this by the prolonged action of boiling water, is converted into *nitrate of diphenyl-trimercurammonium*, $\overset{\prime\prime}{Hg}{}^3(C^6H^5)^2N^2.2NO^3.H^2O$. (Schiff.)

*Nitrate of Phenyl-mercurosammonium*, $Hg(C^6H^5)H^2N.NO^3$, is formed by treating aniline with mercurous nitrate; it is crystalline and easily decomposible. (Schiff.)

PALLADIUM-COMPOUND. *Chloride of Diphenyl-palladammonium*, $Pd''(C^6H^5)^2H^4N^2Cl^2$, is formed on adding palladious chloride to water containing aniline in suspension, as a light yellow crystalline precipitate, insoluble in excess of aniline. A similar precipitate is formed with palladious iodide. (Gerhardt.)

TIN-COMPOUNDS. *Chloride of Diphenylstannosammonium*, $Sn''(C^6H^5)^2H^4N^2.Cl^2$, is formed as a slightly soluble crystalline mass on mixing aniline and stannous chloride in equivalent proportions.

*Chloride of Tetraphenylstannicammonium*, $Sn^{iv}(C^6H^5)^4H^8N^4Cl^4$, is produced by strongly heating an intimate mixture of 2 at. aniline and 1 at. tetrachloride of tin, or by dropping aniline into a solution of the tetrachloride in benzene. It is a white crystalline powder which is decomposed by water with separation of stannic oxide. When heated even in a stream of dry carbonic anhydride, it is resolved, according to Schiff, into aniline, ammonia and rosaniline? (see p. 469).

ZINC-COMPOUNDS.—*Chloride of Diphenyl-zincammonium*, $Zn''(C^6H^5)^2H^4N^2Cl^2$, crystallises in oblique rhombic prisms easily soluble in water and in alcohol, and resolved by prolonged boiling into aniline and chloride of zinc. The *chloroplatinate* is a granulo-crystalline salt. The *bromide* and *iodide* resembles the chloride in composition and properties. The *sulphate*, $Zn''(C^6H^5)^2H^4N^2.SO^4$, is more soluble and serves for the preparation of the preceding salts by double decomposition. (Schiff.)

**PHENYL-AMYL.** $C^{11}H^{16} = C^6H^5.C^5H^{11}$. (Tollens and Fittig, Ann. Ch. Pharm. cxxxi. 313.)—A hydrocarbon formed by the action of sodium on a mixture of bromobenzene (bromide of phenyl) and bromide of amyl, diluted with benzene. The action, which is attended with considerable rise of temperature, is soon completed, and if the mixture be then distilled, a colourless liquid is obtained, containing phenyl-amyl together with traces of free amyl and phenyl, and the benzene used for dilution; and by a few rectifications, collecting apart the liquid which passes over at 193°, the phenyl-amyl may be obtained pure.

Phenyl-amyl is a transparent colourless liquid having a peculiar odour not like that of benzene. It boils at 195°, and has a specific gravity of 0·859 at 12°. By oxidation with *chromate of potassium* and *sulphuric acid*, it is converted into benzoic acid. *Chlorine* attacks it slowly, with evolution of hydrochloric acid, and ultimately converts it into a viscid mass which exhibits no trace of crystallisation. By *fuming nitric acid* it is converted, with great evolution of heat, into nitrophenyl-amyl, $C^{11}H^{15}(NO^2)$, which separates as an oil on addition of water, and cannot be distilled without decomposition. A certain quantity of dinitrophenyl-amyl is however always formed at the same time, and in greater proportion as the temperature is allowed to rise higher. Nitrophenylamyl is easily reduced by *tin* and *hydrochloric acid*, yielding a base in the form of a white flocculent precipitate, which, on exposure to the air, quickly assumes a dark blue colour and decomposes.

Phenyl-amyl dissolves easily at a gentle heat in very strong or in fuming *sulphuric acid*, forming a sulpho-acid, $C^{11}H^{16}SO^3$, which when neutralised with barytic carbonate, yields a *barium-salt*, $C^{22}H^{30}Ba''S^2O^6$, crystallising with great facility in long capillary silky needles, sparingly soluble in cold, somewhat more soluble in hot water. The *potassium-salt*, $C^{11}H^{15}KSO^3$, prepared from the barium-salt by double decomposition, forms a radio-crystalline mass very soluble in water and in alcohol. The *free acid* separated from the barium-salt by sulphuric acid, solidifies in vacuo to a radio-crystalline mass, which deliquesces very quickly on exposure to the air, but forms a crystalline compound with a larger quantity of water. It is a very stable compound, melts when heated, and decomposes only at a much higher temperature. Its aqueous solution may be boiled for a long time and evaporated to a thick syrup without decomposition. On adding *chloride of barium* to a dilute solution mixed with hydrochloric acid, the large needles of the barium-salt are deposited in a few seconds. *Chloride of calcium* forms, only in a concentrated solution of the acid, a precipitate which dissolves on heating the liquid, and separates as it cools in shining crystalline scales. *Nitrate of silver* forms, even in a somewhat dilute solution of the acid, a white precipitate which dissolves in hot water, and crystallises therefrom in large shining needles.

**PHENYL-ANISAMIDE** or *Anisanilide*, $C^{14}H^{13}NO^2 = \left.\begin{matrix}C^8H^7O^2\\C^6H^5\\H\end{matrix}\right\}N$.—Obtained by the action of chloride of anisyl, $C^8H^7O^2Cl$, on aniline. Crystallises from alcohol in slender needles which sublime at a gentle heat. (Cahours, Ann. Ch. Phys. [3] xxiii. 353.)

**PHENYL-ARSENAMIC ACID.** $C^6H^8AsNO^3 = \left.\begin{matrix}H^2.C^6H^5\\(AsO)'''\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$ or perhaps $\left.\begin{matrix}H^2.C^6H^5\\(AsO^2)'\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$ (Béchamp, Compt. rend. lvi. 1172).—When the product obtained by heating arsenate of aniline is treated with a solution of sodic carbonate, carbonic anhydride is evolved, and a viscid precipitate is formed, consisting of aniline and colouring matters, and the filtered solution, when evaporated and mixed with nitric acid, deposits phenyl-arsenamic acid, which may be rendered colourless by crystallisation from water, with addition of animal charcoal. It is decomposed by heat, dissolves without alteration in alkalis, but is decomposed by fusion with alkalis, into aniline and an alkaline arsenate: it decomposes carbonates, forming crystalline salts. The *sodium-salt*, $C^6H^7AsNO^3$, and the *potassium-salt* crystallise in rectangular prisms; the *barium-salt* in oblique prisms. The *silver-salt* is anhydrous and likewise crystallisable. The *lead-* and *copper-salts* are bulky precipitates.

**PHENYL-BENZAMIDES.** Amides containing benzoyl and phenyl or its derived radicles.

**Phenyl-benzamide or Benzanilide,** $C^{13}H^{11}NO = \left.\begin{matrix}C^6H^5\\C^7H^5O\\H\end{matrix}\right\}N$. (Gerhardt,

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Ann. Ch. Phys. [3] xxxvii. 327.)—Produced by the action of chloride of benzoyl, or of benzoic anhydride, on aniline:

$$C^7H^5OCl \quad + \quad C^6H^5.H^2.N \quad = \quad (C^6H^5)(C^7H^5O)HN \quad + \quad HCl.$$
$$(C^7H^5O)^2O \quad + \quad 2(C^6H^5.H^2.N) \quad = \quad 2[(C^6H^5)(C^7H^5O)HN] \quad + \quad H^2O.$$

The product obtained by either of these reactions is washed with water and the residue is purified by recrystallisation from boiling alcohol.

Phenyl-benzamide crystallises in shining scales insoluble in water. Heated with melting *potash*, it is resolved into aniline and benzoate of potassium. When heated with *chloride of benzoyl*, it gives off hydrochloric acid and is converted into phenyl-dibenzamide.

*Phenyl-nitrobenzamide* or *Nitrobenzanilide*, $(C^6H^5)[C^7H^4(NO^2)O]HN$, appears to be formed by the action of aniline on chloride of nitrobenzoyl (i. 568). The action is attended with great rise of temperature and evolution of hydrochloric acid, and the product is a solid body, which crystallises from alcohol in shining needles. (Bertagnini, Ann. Ch. Pharm. lxxix. 269.)

**Phenyl-dibenzamide** or **Dibenzanilide**, $C^{20}H^{15}NO^2 = \left.\begin{matrix}C^6H^5\\(C^7H^5O)^2\end{matrix}\right\}N.$ (Gerhardt and Chiozza, Compt. rend. xxxvii. 90.)—Prepared by heating phenyl-benzamide with chloride of benzoyl, removing the excess of the latter with carbonate of sodium, and recrystallising the residue from boiling alcohol. It forms slender shining needles, sometimes grouped in rounded grains. It is but slightly soluble in cold alcohol of ordinary strength.

**Diphenyl-benzamide**, $C^{19}H^{15}NO = \left.\begin{matrix}(C^6H^5)^2\\C^7H^5O\end{matrix}\right\}N.$ (Hofmann, Ann. Ch. Pharm. cxxxii. 166.)—Produced by heating chloride of benzoyl with diphenylamine. It is a thick oil which solidifies in the crystalline form on cooling. By washing with water and recrystallisation from boiling alcohol, in which it is but slightly soluble, it is obtained in fine crystals.

When treated with cold nitric acid of ordinary strength, it is converted into phenyl-nitrophenyl-benzamide, $\left.\begin{matrix}C^6H^5\\C^6H^4(NO^2)\\C^7H^5O\end{matrix}\right\}N$, a light yellow, easily crystallising compound, which dissolves with scarlet colour in alcoholic soda, and is thereby resolved into benzoic acid and splendid yellow-red, neutral needles of phenyl-nitrophenylamine or nitrodiphenylamine, $\left.\begin{matrix}C^6H^5\\C^6H^4(NO^2)\\H\end{matrix}\right\}N.$

If, on the other hand, diphenylbenzamide be treated with the strongest *fuming nitric acid*, a solution is formed from which water precipitates a deep yellow crystalline mass consisting of dinitrodiphenyl-benzamide, $\left.\begin{matrix}[C^6H^4(NO^2)]^2\\C^7H^5O\end{matrix}\right\}N$, which dissolves in alcoholic potash, forming a solution of a splendid crimson colour, which on addition of water deposits a yellow crystalline powder, while potassic benzoate (?) remains in solution.

The yellow powder, when crystallised from alcohol, yields reddish-yellow needles with blue metallic reflex, consisting of dinitro-diphenylamine, $\left.\begin{matrix}[C^6H^4(NO^2)]^2\\H\end{matrix}\right\}N.$

**Phenyl-tolyl-benzamide** or **Phenyl-benzyl-benzamide**, $C^{20}H^{17}NO = \left.\begin{matrix}C^6H^5\\C^7H^7\\C^7H^5O\end{matrix}\right\}N.$ (Hofmann, Ann. Ch. Pharm. cxxxii. 293.)—Produced by the action of chloride of benzoyl on phenyl-tolylamine (p. 454). The action is brisk, and the product remains fluid for a long time, but when treated with water, alkali, and alcohol, it ultimately solidifies, and when dissolved in boiling alcohol, separates in well-developed crystals which are more soluble than diphenyl-benzamide.

Phenyl-tolyl-benzamide is more easily attacked by nitric acid than the diphenyl-compound. On treating it with ordinary strong nitric acid, the crystals immediately become fluid; and if the addition of nitric acid be continued till they dissolve, and water be then added to the solution, a yellow crystalline precipitate is formed consisting of dinitrophenyl-tolyl-benzamide $\left.\begin{matrix}C^6H^4(NO^2)\\C^7H^6(NO^2)\\C^7H^5O\end{matrix}\right\}N$, which crystallises from boiling alcohol in small yellowish-red needles. This compound dissolves with faint carmine colour in alcoholic soda, being thereby deprived of its benzoyl-atom, and converted into dinitrophenyl-tolylamine, $\left.\begin{matrix}C^6H^4(NO^2)\\C^7H^6(NO^2)\\H\end{matrix}\right\}N.$

Dinitrophenyl-tolyl-benzamide treated with reducing agents is converted into a basic compound which crystallises in beautiful white needles.

Fuming *nitric acid* converts phenyl-tolyl-benzamide into a nitrated amide which appears to contain 5 at. $NO^2$.

**PHENYL-BENZOYL,** $C^{13}H^{10}O = C^6H^5.C^7H^5O$.—This body, the ketone of benzoic acid, has been already described as Benzone or Benzophenone (i. 562). It was discovered by Péligot, and has been further examined by Chancel, and recently by Linnemann (Ann. Ch. Pharm. cxxxiii. 1). It crystallises, according to Handel, in orthorhombic prisms exhibiting the combination $\bar{P}\infty . \breve{P}\infty . \infty P . \frac{1}{2}\bar{P}\infty . P . oP$. Ratio of principal to secondary axes = 1 : 0·8496 : 0·6535. Angles $\infty P : \infty P$ = 80° 42′ and 99° 18′. It melts at 48° to 48·5° and boils at 295° under a pressure of 0·741 mm. (compare Chancel's determinations, i. 562). Vapour-density, obs. = 6·22 (Linnemann); calc. (2 vols.) = 6·28.

Benzophenone heated with excess of *bromine* in sealed tubes to 150°, is converted, with separation of hydrobromic acid, into a brominated compound containing 41·39 per cent. carbon, 2·08 hydrogen and 52·18 to 52·23 bromine, probably therefore $C^{26}H^{16}Br^4O^2$ which requires 41·10 carbon, 1·97 hydrogen, 52·70 bromine and 4·21 oxygen. It dissolves in boiling alcohol, and separates on cooling as a snow-white silky mass composed of microscopic needles. It melts at 125°, cannot be distilled without decomposition, and yields with sodium-amalgam an oil free from bromine. (Linnemann.)

Benzophenone treated in alcoholic solution with *sulphuric acid* and *zinc*, is converted by the nascent hydrogen into benzopinacone, a substance related to benzophenone in the same manner as pinacone, $C^6H^{14}O^2$, to acetone:

$$\underset{\text{Benzophenone.}}{2C^{13}H^{10}O} + H^2 = \underset{\text{Benzopinacone.}}{C^{26}H^{22}O^2}.$$

The benzopinacone is very slightly soluble in alcohol and is deposited on the zinc in the form of a white crust (see Pinacone.)

When, on the other hand, benzophenone dissolved in alcohol is treated with *sodium-amalgam*, a different reaction takes place, resulting in the formation of benzhydrol, $C^{13}H^{12}O = \left.\begin{matrix}C^{13}H^{11}\\H\end{matrix}\right\}O$, a monatomic alcohol capable of exchanging its typic hydrogen for alcohol- and acid-radicles:

$$C^{13}H^{10}O + H^2 = C^{13}H^{12}O.$$

**Benzhydrol.** This body is sparingly soluble in *water*, 1 part of it requiring for solution 2000 pts. of water at 20°; but in *alcohol*, *ether*, *chloroform*, *benzene* or *sulphide of carbon*, it dissolves with facility, and crystallises therefrom in groups of slender silky needles. It dissolves in alkaline liquids more easily than in pure water; a concentrated solution of caustic potash saturated with benzhydrol, deposits the compound in the crystalline form on addition of water or neutralisation with an acid. Benzhydrol melts between 167·5° and 168°, and boils between 297° and 298° under a pressure of 748 mm.

Benzhydrol heated with dilute aqueous *chromic acid*, is reconverted into benzophenone. *Fuming nitric acid* converts it into dinitrobenzophenone, $C^{13}H^8(NO^2)^2O$, which crystallises from boiling alcohol in needles having a faint chamois-colour and melting at 129°. With bromine it yields dibromobenzhydrol, $C^{13}H^{10}Br^2O$, which crystallises from alcohol in a light mass of white microscopic needles becoming soft at about 158° and melting at 163°.

Benzhydrol is resolved, partially by distillation or by heating to 300° in sealed tubes, and completely by prolonged boiling under the ordinary pressure, into water and benzhydrolic ether, $C^{26}H^{22}O = 2C^{13}H^{12}O - H^2O$.[*] The same dehydration, resulting in the formation of benzhydrolic ether, is effected by the action of chloride or iodide of phosphorus.

*Benzhydrolic ether* separates from solution in boiling alcohol in plumose tufts of microscopic crystals; it dissolves easily in *benzene* and separates therefrom by spontaneous evaporation in very small but distinct crystals; and by immersing one of these in the solution during evaporation, larger crystals may be obtained which exhibit the form of monoclinic prisms, $+P . -P . -P\frac{1}{2} . (\infty P\infty) . \infty P\infty$. Ratio of clinodiagonal, orthodiagonal and principal axes = 0·6820 : 1 : 0·523. Angle of inclined axes = 81° 25′. It melts at 111°, remaining liquid for a long time after cooling; begins to volatilise above 300° and boils at 315° under a pressure of 745 mm. It dissolves in *fuming nitric acid*, and is decomposed thereby on heating, yielding a nitrogenous product; also in strong *sulphuric acid*.

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[*] This is the first known instance of the conversion of a monatomic alcohol into the corresponding anhydride or ether by the action of heat alone.

*Benzhydrolic Ethylate*, $\left.\begin{matrix}C^{13}H^{11}\\C^{2}H^{5}\end{matrix}\right\}O$, is produced by mixing a solution of benzhydrol in absolute alcohol with $\frac{1}{10}$th of its volume of strong sulphuric acid, avoiding rise of temperature, and leaving the liquid to itself for several days. On then adding water, the ether separates as an oil, which may be purified by washing with dilute potash and with water, and subsequent rectification. It is an inodorous syrupy liquid, of specific gravity 1·029 at 20°, and boiling at 183° under a pressure of 736 mm. It is strongly refractive, and when newly prepared quite colourless; but by exposure to diffused daylight for some time, or to direct sunshine for a few seconds, it becomes coloured, appearing of a fine green colour by reflected and faintly yellow by transmitted light. The colour is destroyed by leaving the liquid for some time in the dark, or by gentle heating, or by agitation, but may be restored by exposure to light. After keeping for a few months, however, the colour disappears altogether, and is no longer restored even by exposure to bright sunshine. In either state, the liquid exhibits strong fluorescence when a beam of light is transmitted through it in a dark room, the emergent light being of a bright light blue colour. Benzhydrolic ethylate dissolves in twenty times its volume of *alcohol* of 80 per cent., and in all proportions of *ether* and *benzene*. It is not altered by distillation with concentrated hydriodic acid. When fused with *potash* it gives off a gas burning with a smoky flame, and is converted into an acid which is precipitated on neutralising the alkali with hydrochloric acid, but redissolves with facility in caustic potash or carbonate of potassium.

*Benzhydrolic Acetate*, $C^{15}H^{14}O^{2} = \left.\begin{matrix}C^{2}H^{3}O\\C^{13}H^{11}\end{matrix}\right\}O$.—Produced by boiling benzhydrol for several hours with glacial acetic acid. It is precipitated by water and purified like the preceding compound. It is an inodorous viscid liquid of specific gravity 1·49 at 20°, colourless when first prepared, but affected by light exactly in the same manner as the ethyl-compound. It remains liquid at 150°, boils at 301—302° under a pressure of 731 mm.; dissolves easily in *alcohol*, *ether*, and *benzene*. *Alcoholic potash* decomposes it, even at ordinary temperatures, into acetic acid and benzhydrol.

*Benzhydrolic Benzoate*, $\left.\begin{matrix}C^{7}H^{5}O\\C^{13}H^{11}\end{matrix}\right\}O$.—Produced by fusing 3 pts. benzhydrol with 2 pts. benzoic acid, continuing the heat till the mass begins to boil quietly, dissolving the cooled product in ether, agitating with potash, and evaporating. The residue is then pulverised, washed with alcohol, dissolved in ether, and the solution is mixed with an equal volume of alcohol and left to evaporate. This compound is not produced by treating benzhydrol with chloride of benzoyl, which indeed acts just like chloride of phosphorus, producing nothing but benzhydrolic oxide.

Benzhydrolic benzoate forms trimetric crystals in which the principal is to the secondary axes as 1 : 0·4770 : 0·6682. They are usually four-sided prisms, $\infty P$, with angles of 61° and 129°, and terminated by a brachydome $\breve{P}\infty$ with angles of 67° 30′ and 112° 30′. It melts between 87·5° and 89°; dissolves easily in *ether* and *benzene*, sparingly in cold, more easily in hot *alcohol*. It is decomposed by distillation, leaving a carbonaceous residue and yielding a distillate containing benzoic acid, benzoic anhydride, an oily body slightly soluble in cold alcohol, and a small quantity of a hydrocarbon, $C^{13}H^{10}$. By evaporation with *alcoholic potash-solution*, it is completely resolved into benzoic acid and benzhydrol.

*Benzhydrolic Succinate*, $C^{30}H^{26}O^{4} = \left.\begin{matrix}(C^{4}H^{4}O^{2})''\\(C^{13}H^{11})^{2}\end{matrix}\right\}O^{2}$.—Produced, similarly to the preceding, by fusing an intimate mixture of 30 pts. benzhydrol and 9 pts. succinic acid. It separates from boiling alcohol as a very light mass of small shining scales; melts at 141°—142°, and solidifies on cooling to a transparent amorphous mass, immediately becoming crystalline when gently heated. It is insoluble in *water*, sparingly soluble in cold *alcohol*, *ether*, and *benzene*, more easily when heated. It burns with a smoky flame, leaving no residue. By *alcoholic potash* at the boiling heat, it is completely resolved into succinic acid and benzhydrol. By *distillation* it is partly resolved into succinic acid and a hydrocarbon $C^{13}H^{10}$, which may be called benzhydrolene:

$$C^{30}H^{26}O^{4} = C^{4}H^{6}O^{4} + 2C^{13}H^{10}.$$

Another kind of decomposition appears, however, to take place at the same time, for the quantity of benzhydrolene obtained is but small, and it is accompanied by a considerable quantity of an oily product.

To prepare benzhydrolene, benzhydrolic succinate, or a mixture of succinic acid and benzhydrol is repeatedly distilled; the semisolid distillate is freed from liquid products by cold alcohol, from succinic acid by potash, and from undecomposed benzhydrolic succinate by treatment with alcoholic potash, and the residual product is crystallised from boiling benzene. It is also produced, as already observed, by the dry distillation of benzhydrolic benzoate.

Benzhydrolene melts at 209°—210°. It is nearly insoluble in cold *alcohol*, and only slightly soluble in boiling alcohol, from which it is deposited in small needles on cooling. It dissolves sparingly also in *ether*, but easily in hot *benzene*, whence it crystallises for the most part on cooling. It does not combine with picric acid. (Linnemann.)

**PHENYL-BENZYLAMINE.** Syn. with PHENYL-TOLYLAMINE, or TOLYL-ANILINE (p. 454).

**PHENYL-BENZYLENAMINE,** or rather DIPHENYL-DIBENZYLENE-DIAMINE or DIPHENYL-DITOLYLENE-DIAMINE, $(C^6H^5)^2(C^7H^6)''^2N^2$ (see page 458).

**PHENYL-BROMIMESATIN.** See PHENYL-IMESATINS (p. 485).

**PHENYL-BUTYRAMIDE.** $C^{10}H^{13}NO = \left.\begin{matrix}C^4H^7O\\C^6H^5\\H\end{matrix}\right\}N$. (Gerhardt, Ann. Ch. Phys. [3] xxxvii. 329.)—Produced by the action of aniline on butyric anhydride or chloride of butyryl. It is insoluble in water, but easily soluble in alcohol and ether, and crystallises from weak boiling spirit in beautiful nacreous laminæ. It melts at 90°, and distils without alteration. It is scarcely attacked by boiling potash-ley, but gives off aniline when fused with hydrate of potassium.

**PHENYL-CARBAMIC ACID.** See CARBAMIC ACID (i. 751).

**PHENYL-CARBAMIDES.** See CARBAMIDE (i. 755).

**PHENYL-CETYLAMINE** or *Cetylaniline*. (See PHENYLAMINES, p. 450.)

**PHENYL-CHLORIMESATIN.** See PHENYLIMESATINS (p. 485).

**PHENYL-CHLOROCYANAMIDE.** See PHENYLAMINES (p. 442).

**PHENYL-CINNAMIDE.** See CINNAMIDE (i. 989).

**PHENYL-CITRACONAMIDES.** See CITRACONIC ACID, AMIDES OF (i. 993).

**PHENYL-CITRAMIDES.** See CITRIC ACID, AMIDES OF (i. 1000).

**PHENYL-DIAMINES.** See PHENYLAMINES (p. 454).

**PHENYLENE.** $C^6H^4$.—A liquid having this composition and boiling at 91° was found by Church (p. 415) among the products of the distillation of phenylic chloride with sodium-amalgam.

**PHENYLENE-DIAMINE.** $C^6H^8N^2 = \left.\begin{matrix}(C^6H^4)''\\H^4\end{matrix}\right\}N^2$. (Hofmann, Proc. Roy. Soc. xi. 518; xii. 639.)—This base is obtained by the action of reducing agents on nitraniline:

$$C^6H^6(NO^2)N + H^6 = C^6H^8N^2 + 2H^2O,$$

and exhibits the isomeric modifications α and β, according as it is produced from α- or β-nitraniline.

Alpha-phenylene-diamine is easily prepared by the action of ferrous acetate on α-nitraniline, or by the prolonged action of the same reagent on dinitrobenzene, that compound being converted, first into nitraniline, and then, by a continuation of the same action, into phenylene-diamine:

$$\underset{\text{Dinitrobenzene.}}{\left.\begin{matrix}C^6H^4NO^2\\NO^2\end{matrix}\right\}} \qquad \underset{\text{Nitraniline.}}{\left.\begin{matrix}C^6H^4NO^2\\NH^2\end{matrix}\right\}} \qquad \underset{\text{Phenylene-diamine.}}{\left.\begin{matrix}C^6H^4NH^2\\NH^2\end{matrix}\right\}}$$

The substance called semibenzidam, which Zinin (J. pr. Chem. xxxiii. 44) obtained by the prolonged action of sulphide of ammonium on dinitrobenzene, sometimes in brown flakes, sometimes as a yellow resin, exhibiting the composition $C^6H^8N^2$, was probably impure α-phenylene-diamine.

Beta-phenylene-diamine, the product of the reduction of β-nitraniline (obtained from nitrophenyl-acetamide, &c., p. 418), may also be prepared by two other processes, viz.,

*a.* By the action of ferrous acetate on dinitraniline:

$$C^6H^5(NO^2)^2N + 7H^2 = C^6H^8N^2 + NH^3 + 4H^2O$$

*b.* By the action of zinc and sulphuric acid, or other powerful reducing agents, on dinitrazobenzene (i. 478), or diphenine, $C^6H^6N^2$ (ii. 336), which is the first product of the same kind of action on dinitrazobenzene:

$$\underset{\text{Dinitrazobenzene.}}{C^{12}H^8N^2(NO^2)^2} + 6H^2 = 4H^2O + \underset{\text{Diphenine.}}{2C^6H^6N^2}.$$

$$\underset{\text{Diphenine.}}{C^6H^6N^2} + H^2 = \underset{\text{Phenylene-diamine.}}{C^6H^8N^2}.$$

*Properties.*—Alpha-phenylene-diamine when freshly distilled is a slightly coloured heavy oil which, like aniline, has a tendency to assume a brown colour on exposure to the air. It often remains liquid for days, and then gradually solidifies to a mass of crystals which become hard and white by washing with ether. It melts at 63°, boils at near 287°, and distils without decomposition. It is very soluble in *water* and in *alcohol*, forming solutions which have a distinctly alkaline reaction; much less soluble in *ether*.

Beta-phenylene-diamine crystallises much more readily than the α-base. It melts at 140°, boils at 267°, and sublimes even below its boiling point, in splendid crystalline plates resembling pyrogallic acid.

A solution of β-phenylene-diamine in sulphuric acid mixed with peroxide of manganese yields quinone, which distils over on heating the mixture and crystallises in the receiver:

$$\underset{\beta\text{-phenylene-diamine.}}{C^6H^8N^2} + 2H^2SO^4 + Mn''O^2 = \underset{\text{Quinone.}}{C^6H^4O^2} + Mn''SO^4 + (NH^4)^2SO^4.$$

Alpha-phenylene-diamine when similarly treated evolves a faint odour of quinone, but does not yield crystals.

Both modifications of phenylene-diamine are di-acid and form salts which crystallise easily and well. The β-salts are more soluble than the α-salts. β-phenylene-diamine and its salts are remarkable for the facility with which they are converted into violet and blue compounds under the influence of oxidising agents, such as chlorine, bromine, chromic acid, ferric and platinic chloride, &c. The salts of both modifications are easily decomposed by the fixed caustic alkalis, the β base crystallising immediately, whereas the α base separates in oily globules which only gradually solidify. The base is also separated from its salts by ammonia, but redissolves in excess, forming a solution which gradually turns brown and decomposes. This may perhaps explain why the diamine cannot be conveniently obtained from dinitrobenzene by reduction with sulphide of ammonium.

*Hydrochlorate of α-phenylene-diamine*, $C^6H^8N^2.2HCl$ or $(C^6H^4)''H^6N^2Cl^2$, is very soluble in water, but crystallises easily from concentrated hydrochloric acid. The *β-hydrochlorate* is also extremely soluble in water, sparingly in hydrochloric acid, and crystallises in large prisms. The *α-chloroplatinate*, $C^6H^{10}N^2Cl^2.Pt^{iv}Cl^4$, crystallises in splendid needles. The *β-salt* of the same composition forms light yellow plates extremely soluble in water and easily decomposed by heat.

The *β-hydrobromate*, $C^6H^8N^2.2HBr$, resembles the hydrochlorate in every respect. The *α-hydrobromate* and *α-hydriodate* separate immediately in crystalline masses on bringing the base in contact with the respective acids; they crystallise splendidly from water and more especially from alcohol. The *nitrate*, *oxalate*, and *sulphate* also crystallise well.

Both α- and β-phenylene-diamine are readily attacked by the alcoholic iodides. By alternate treatment with iodide of methyl and oxide of silver (or distillation with soda) twice repeated, and one more treatment with iodide of methyl, each base yields a well crystallised iodide containing $C^{12}H^{22}N^2I^2 = \left.\begin{matrix}(C^6H^4)'' \\ (CH^3)^4\end{matrix}\right\}N^2.2CH^3I$, or iodide of hexmethyl-phenylene-diammonium $\left[\left.\begin{matrix}(C^6H^4)'' \\ (CH^3)^6\end{matrix}\right\}N^2\right]''I^2$, crystallising in plates extremely soluble in water, less soluble in alcohol. It exhibits the same properties whether prepared from α- or from β-phenylene-diamine, excepting that the β compound is the more soluble of the two.

Intermediate compounds may of course be obtained by stopping the action at an earlier stage. β-tetramethyl-phenylene-diamine, $\left.\begin{matrix}C^6H^4 \\ (CH^3)^4\end{matrix}\right\}N^2$, treated with methylic iodide yields, before being converted into the hexmethylated compound above mentioned, a rather difficultly soluble pentamethylated iodide containing $C^{11}H^{19}N^2I = \left.\begin{matrix}(C^6H^4)'' \\ (CH^3)^4\end{matrix}\right\}N^2.CH^3I$; and this, when treated with hydriodic acid, is converted into the di-iodide of pentamethyl-phenylene-diammonium, $C^{11}H^{20}N^2I^2 = \left[\left.\begin{matrix}(C^6H^4)'' \\ (CH^3)^5H\end{matrix}\right\}N\right]''I^2$.

### *Derivatives of Phenylene-diamine.*

**Nitrophenylene-diamine,** $C^6H^7N^3O^2 = \left.\begin{matrix}[C^6H^3(NO^2)]'' \\ H^4\end{matrix}\right\}N^2$. *Azophenylamine*

(Gottlieb). *Nitrazophenylamine* (Gerhardt).—This compound, discovered by Gottlieb (Ann. Ch. Pharm. lxxxv. 27), is produced by the action of sulphide of ammonium on dinitraniline:

$$C^6H^5(NO^2)^2N + 3H^2S = C^6H^7N^3O^2 + 2H^2O + S^2.$$

When dinitraniline is boiled for about two hours with a large excess of solution of sulphide of ammonium, the liquid acquires a dark red colour, and the crystals of dinitraniline disappear, being succeeded by a network of delicate shining dark red needles, which gradually increase in quantity, and are likewise abundantly deposited after the action is completed and the liquid has cooled. The compound is obtained pure by precipitating it from the hydrochlorate or oxalate purified by several crystallisations, and then recrystallising it two or three times from hot alcohol.

Nitrophenylene-diamine crystallises in groups of long slender needles having a slight red colour when dry, and exhibiting a golden iridescence on their broader faces. When separated by ammonia from a saturated solution of one of its salts, it takes the form of a dull brick-red powder; but dilute solutions deposit it in small, reddish-yellow, shining plates. It melts at a high temperature and volatilises in great part without decomposition, forming a woolly sublimate. When suddenly heated, it explodes slightly, leaving a residue of charcoal. It dissolves readily in water, alcohol and ether, forming deep red solutions.—*Nitrous acid* converts it into azonitrophenylenic acid (p. 484).

It combines with *acids*, forming mono-acid salts which are decomposed by water and by alcohol, with separation of the base: hence in preparing them, it is necessary to let them crystallise in presence of an excess of acid.

*Sulphate of Nitrophenylene-diamine*, $(C^6H^7N^3O^2)^2H^2SO^4$, is obtained by dissolving the base in warm dilute sulphuric acid, and separates on cooling in yellowish scales, having a fatty lustre and containing 8·20 per cent. sulphur.

A mixture of the solution of this salt with sulphate of alumina, does not yield any double salt when left to evaporate.

*The Hydrochlorate*, $C^6H^7N^3O^2.HCl.H^2O$, may be prepared by boiling the crude base with dilute hydrochloric acid, which dissolves it, leaving only a residue of sulphur and a secondary product of a dull green crystalline aspect, part of which also passes into the solution. To free the salt completely from this impurity, it must be repeatedly dissolved in boiling dilute hydrochloric acid and recrystallised. From a concentrated acid solution, it separates in yellowish-brown needles; from a dilute solution by spontaneous evaporation, in oblique prisms often four or five millimetres in length and united in groups. These crystals exhibit a light brownish-green colour by transmitted light, and a peculiar blue iridescence on some of their faces by reflected light. The acid solution has a greenish-brown colour. The crystals contain 1 at. water which they give off at 100°, or in vacuo or over oil of vitriol at ordinary temperatures. At 100°, however, partial decomposition takes place and hydrochloric acid is given off.

*Chloroplatinate*, $2(C^6H^7N^3O^2.HCl)PtCl^4$.—A dilute solution of the hydrochlorate mixed with tetrachloride of platinum, does not yield a double-salt, the platinum being reduced to the metallic state (Gottlieb); but on adding the chloride of platinum to a concentrated solution of the hydrochlorate, the chloroplatinate is obtained in splendid long brown-red prisms. (Hofmann, Proc. Roy. Soc. x. 499.)

*Cyanoplatinate*, $2(C^6H^7N^3O^2.HCy).PtCy^4.\frac{5}{2}H^2O$.—Obtained by adding the crystallised hydrochlorate of nitrophenylene-diamine to a boiling aqueous solution of platinocyanide of magnesium. The solution separated by filtration from a small quantity of dark insoluble matter, gradually deposits a mixture of the cyanoplatinate and the free base, which latter may be removed by digestion with a small quantity of dilute hydrochloric acid. It forms large laminæ, having a light brownish-yellow colour and strong lustre, and giving of their water at 112°. They cannot be recrystallised from water without partial decomposition.

*Nitrate*, $C^6H^7N^3O^2.NHO^3$.—Warm dilute nitric acid readily dissolves nitrophenylene-diamine, but the solution soon acquires a dark colour and deposits flakes, indicating partial decomposition. The pure salt may however be obtained by moistening the base with water, and pouring dilute nitric acid upon it by small portions: it is then immediately converted into a thick magma of micaceous scales, which may be freed from the mother-liquor by pressure between paper. The salt thus prepared is anhydrous, and may be kept for months over oil of vitriol without losing its lustre.

*Oxalate*, $2C^6H^7N^3O^2.C^2H^2O^4$.—Obtained by dissolving the base in aqueous oxalic acid. From concentrated solutions it separates in yellow needles; from more dilute solutions, in brownish-yellow prisms, exhibiting a bluish iridescence on certain faces. It is anhydrous, and dissolves but sparingly in cold water.

The *sulphate*, $2C^6H^7N^3O^2.H^2SO^4$, is obtained by dissolving the base in warm dilute sulphuric acid, and separates on cooling in yellowish scales having a fatty lustre.

NITROPHENYLENE-OXAMIDE, $C^8H^5N^3O^4 = \left.\begin{matrix}(C^2O^2)'' \\ [C^6H^3(NO^2)]'' \\ H^2\end{matrix}\right\}N^2$. *Oxalazophenylamide* (Gottlieb). *Nitrazophenyl-oxamide* (Gerhardt).—When nitrophenylene-diamine is dissolved in excess of oxalic acid, and the liquid is evaporated over the water-bath, a brownish-green residue is obtained, consisting partly of nitrophenylene-oxidiamic acid, and partly of nitrophenylene-oxamide:

$$\underset{\text{Acid oxalate of Nitrophenylene-diamine.}}{C^6H^7N^3O^2.C^2H^2O^4} - H^2O = \underset{\text{Nitrophenylene-oxidiamic-acid.}}{C^8H^7N^3O^5},$$

and: $$C^8H^7N^3O^5 - H^2O = \underset{\text{Nitrophenylene-oxamide.}}{C^8H^5N^3O^4}.$$

If kept for some time at 100° it is almost wholly converted into the latter compound, without change of aspect. (Gottlieb, Ann. Ch. Pharm. lxxxv. 38.)

NITROPHENYLENE-OXIDIAMIC ACID, $C^8H^7N^3O^5 = \left.\begin{matrix}H^3[C^6H^3(NO^2)]'' \\ (C^2O^2)'' \\ H\end{matrix}\right\}\begin{matrix}N^2 \\ O\end{matrix}$. *Oxalazophenylamic acid* (Gottlieb). *Nitrazophenyl-oxamic acid* (Gerhardt).—The ammonium-salt of this acid is obtained by treating the brownish-green residue above-mentioned with aqueous ammonia. It is sparingly soluble, and crystallises from a hot aqueous solution in yellow needles. The *barium-salt*, $C^{16}H^{12}Ba''N^6O^{10}.3H^2O$, is obtained as a light orange-coloured, sparingly soluble, crystalline precipitate on mixing the ammonium-salt with chloride of barium. It retains 3 at. water at 100°, and becomes anhydrous at 160°. By decomposing this salt with hydrochloric acid, the free acid is precipitated in small light-yellow granular crystals. (Gottlieb, *loc. cit.*)

**Azophenylene-diamine,** $C^6H^5N^3 = \left.\begin{matrix}(C^6H^4)'' \\ N''' \\ H\end{matrix}\right\}N^2$, or *Diazobenzolimide*, $\left.\begin{matrix}(C^6H^4N^3)'' \\ H\end{matrix}\right\}N$. (Griess, Phil. Trans. 1864, [3] 682.)—This compound is produced by the action of aqueous ammonia on perbromide of azophenylammonium:

$$C^6H^5N^3Br^3 + 4NH^3 = C^6H^5N^3 + 3NH^4Br.$$

The action is attended with considerable evolution of heat, bromide of ammonium passing into solution, and azophenylene-diamine separating as a heavy brown oil, which may be nearly decolorised by repeated distillation with water, then dried over chloride of calcium, and finally redistilled under diminished pressure.

Azophenylene-diamine is remarkable for its narcotic aromatic-ammoniacal odour. It volatilises by distillation with water, or when heated in a vacuum, but on attempting to distil it under the ordinary atmospheric pressure it decomposes with explosive violence. It is not solidified by a frigorific mixture of nitre and sal-ammoniac. Alcohol and ether dissolve it with some difficulty. Hydrochloric acid even when concentrated, and aqueous potash have no action upon it. Strong nitric and sulphuric acids dissolve it without decomposition. Nascent hydrogen, generated by zinc and sulphuric acid in an alcoholic solution of the diamine, reduces it to aniline and ammonia:

$$C^6H^5N^3 + H^6 = C^6H^7N + 2NH^3.$$

**Azobromophenylene-diamine,** $C^6H^4BrN^3 = \left.\begin{matrix}(C^6H^3Br)'' \\ N''' \\ H\end{matrix}\right\}N^2$, or *Diazobromobenzolimide*, $\left.\begin{matrix}(C^6H^3BrN^2)'' \\ H\end{matrix}\right\}N$. (Griess, Phil. Trans. 1864 [3] 700.)—Perbromide of azobromo-phenylammonium (p. 437) is converted by aqueous ammonia into a yellowish oil which by a single distillation with water yields pure azobromophenylenediamine. This compound generally forms a white or slightly yellowish mass of small crystalline plates which melt at 20° to a heavy oil. It is insoluble in water, rather sparingly soluble in alcohol, easily soluble in ether and benzene. It distils readily in presence of water, but explodes feebly when distilled alone. When exposed to the air it appears to volatilise gradually, emitting the same aromatic ammoniacal odour as azophenylene-diamine. It resembles the latter moreover in its behaviour with various reagents; caustic potash, hydrochloric acid and bromine have no action upon it; strong sulphuric and nitric acids decompose it readily.

Nascent hydrogen generated by zinc and sulphuric acid in an alcoholic solution of the diamine, converts it into bromaniline and ammonia:

$$C^6H^4BrN^3 + H^6 = C^6H^6BrN + 2NH^3.$$

By acting upon perbromide of azobromophenylammonium with ethylamine, aniline, &c., corresponding substitution products of azobromophenylene-diamine are obtained.

*Ethyl-azo-bromophenylene-diamine*, $\left.\begin{matrix}(C^6H^3Br)''\\ N'''\\ C^2H^5\end{matrix}\right\}N^2$, forms a yellowish oil which does not solidify even when cooled much below 0°.

The corresponding *phenyl-compound*, $\left.\begin{matrix}(C^6H^3Br)''\\ N'''\\ C^6H^5\end{matrix}\right\}N^2$, forms orange-yellow crystals.

**Azodibromophenylene-diamine,** $\left.\begin{matrix}(C^6H^2Br^2)''\\ N'''\\ H\end{matrix}\right\}N^2$, is produced by the action of aqueous ammonia on perbromide of azodibromo-phenylammonium, and after repeated crystallisation from alcohol, forms white needles which melt at 62°, and detonate slightly at a higher temperature. It is very little soluble in water, more soluble in hot alcohol, easily in ether. (Griess.)

**Azochlorophenylene-diamine,** $\left.\begin{matrix}(C^6H^3Cl)''\\ N'''\\ H\end{matrix}\right\}N^2$, forms easily fusible crystals.

**Azo-iodo-phenylene-diamine,** $\left.\begin{matrix}(C^6H^3I)'''\\ N'''\\ H\end{matrix}\right\}N^2$, forms yellowish-white crystals which are easily fusible, and pass over on distillation with water as a yellowish oil which soon solidifies. It has an aromatic ammoniacal odour like that of the analogous compounds previously described.

**Azo-nitro-phenylene-diamine,** $C^6H^4N^4O^2 = \left.\begin{matrix}[C^6H^3(NO^2)]''\\ N'''\\ H\end{matrix}\right\}N^2$. *Diazonitrobenzolimide.* (Griees, Phil. Trans. 1864, [3] 708, 710.)—This compound, like nitraniline and all its other derivatives, exists in two isomeric modifications, which are obtained by the action of aqueous ammonia on the perbromides of α- and β-azonitrophenylammonium. The α-compound crystallises in orange-coloured needles which melt at 52°. It is somewhat soluble in hot water, from which it crystallises on cooling in whitish needles. It has somewhat of the odour of nitrobenzene.

The β-compound is obtained by repeated crystallisation from hot alcohol in very brilliant yellow, rounded plates, which are so soluble in hot alcohol that a saturated solution deposits a magma of crystals on cooling; they also dissolve as readily in ether. In boiling water they melt, forming a yellow oil but slightly soluble in water, the dissolved portion yielding very fine, almost white crystals on cooling. The crystals obtained by recrystallisation from alcohol melt at 71°, a temperature much higher therefore than the melting point of the α-compound. The β-compound explodes when heated a little above its melting point.

**Azonitrophenylenic acid.** (Hofmann, Proc. Roy. Soc. x. 496.)—This acid, isomeric or metameric with azonitrophenylene-diamine, is produced by the action of nitrous acid on nitrophenylene-diamine, the change consisting, as in other cases of nitrous substitution, in the replacement of 3 at. hydrogen by 1 at. nitrogen:

$$C^6H^7N^3O^2 + NHO^2 = 2H^2O + C^6(H^4N''')N^3O^2.$$

On passing a current of nitrous acid gas into a moderately concentrated solution of nitrate of nitrazophenylene-diamine, the liquid becomes slightly warm, and on cooling deposits a considerable quantity of brilliant white needles, which are sparingly soluble in cold, easily in boiling water, and may be purified by two or three recrystallisations.

The acid thus purified forms long prismatic crystals, often interlaced, white as long as they are immersed in the liquid, but assuming a slightly yellowish tint when dried, especially at 100°; they dissolve readily in alcohol and in ether. It melts at 211° and sublimes in prismatic crystals with partial decomposition at a somewhat higher temperature. It is remarkably stable and may be boiled either with potash or with hydrochloric acid without undergoing any change; neither is it decomposed by passing nitrous acid gas into the aqueous or alcoholic solution.

The crystals have a distinct acid reaction, and dissolve at a gentle heat in potash or ammonia, without however neutralising these liquids. The acid also dissolves in alkaline carbonates, but without expelling the carbonic acid. The *potassium-salt* contains $C^6H^3KN^4O^2$, and the *silver-salt* $C^6H^3AgN^4O^2$.

**PHENYL-DISULPHO-DIAMIC ACID.** See SULPHAMIC ETHERS.

**PHENYL-ETHYL.** $C^8H^{10} = C^6H^5.C^2H^5$. (Tollens and Fittig, Ann. Ch. Pharm. cxxxi. 310.—Fittig, *ibid.* cxxxiii. 222.)—This compound, isomeric, but not identical, with xylene (*q. v.*), is obtained by the action of sodium on a mixture of bromobenzene (bromide of phenyl) and bromide of ethyl, diluted with pure ether. The action is rather energetic and requires to be moderated by external cooling. The distillate after being freed from ether consists almost wholly of phenyl-ethyl, with only traces of free ethyl and phenyl.

Phenyl-ethyl is a colourless mobile liquid, very much like toluene and boiling at 133°. By oxidation with *chromate of potassium* and *sulphuric acid* it is converted into benzoic acid (xylene treated in the same manner yields terephthalic acid, $C^8H^6O^4$).

*Bromine* acts slowly on phenyl-ethyl, with rise of temperature and evolution of hydrobromic acid, and forms a heavy colourless transparent liquid, boiling at 200°, and exhibiting the composition of monobromophenyl-ethyl, $C^8H^9Br$. Heated in sealed tubes with excess of bromine, it is converted into a heavy viscid oil consisting of a mixture of several more highly brominated compounds.

Phenyl-ethyl treated with *fuming nitric acid* in a vessel externally cooled is converted into mononitrophenyl-ethyl, $C^8H^9(NO^2)$, which when precipitated by water and purified by washing, drying over chloride of calcium, and rectification, forms a light yellow oil heavier than water and boiling without decomposition at 233° (nitroxylene is decomposed by distillation). It is easily reduced by *tin* and *hydrochloric acid*, yielding the hydrochlorate of a base which in the free state forms a colourless oil, turning brown on exposure to the air, but not solidifying. The *oxalate* of this base crystallises in large colourless needles, only slightly soluble in cold water. The *chloroplatinate* crystallises in shining scales.

Dinitrophenyl-ethyl, $C^8H^8(NO^2)^2$, is produced by heating the mononitro-compound with nitric acid, or when phenyl-ethyl is gradually dropped into a mixture of 2 vol. strong sulphuric and 1 vol. fuming nitric acid, and the clear liquid is gently heated. It then separates on the surface as a yellow oil which cannot be distilled, but may be purified by washing with water, solution in alcohol, and drying over sulphuric acid. It then forms a light yellow, perfectly transparent oil, which dissolves in boiling alcohol, separates almost completely on cooling, and is decomposed by distillation.

Trinitrophenyl-ethyl, $C^8H^7(NO^2)^3$, is produced in small quantity in the preparation of the dinitro-compound, as above described; and the latter may be almost wholly converted into the trinitro-compound by dissolving it in a mixture of strong sulphuric and fuming nitric acid, boiling the liquid for an hour with repeated addition of fuming nitric acid, then adding sufficient fuming nitric acid to dissolve the oil which has risen to the surface, leaving the solution to itself for 24 hours, and then pouring it into water. The trinitro-compound thus prepared is an oil resembling the dinitro-compound, but still more viscid, and exhibiting no traces of crystallisation, even after long standing. (Xylene is easily converted by fuming nitric acid, even in the cold, into a crystalline trinitro-compound.) It is reduced by sulphide of ammonium to a base, probably $\left.\begin{matrix}[C^8H^7(NO^2)]''\\ H^4\end{matrix}\right\}N^2$, which crystallises from boiling water in orange-yellow laminæ, and forms a hydrochlorate easily soluble in water, alcohol and ether.

Phenyl-ethyl dissolves quickly in gently heated *fuming sulphuric acid*, and the solution if left to itself for some time, deposits slender colourless needles of a sulpho-acid, $C^8H^{10}SO^3$, very deliquescent, having a strongly acid and bitter taste, melting when heated, and blackening at a higher temperature. The same solution neutralised with carbonate of barium yields a very stable *barium-salt*, $C^{16}H^{18}Ba''S^2O^6$, which crystallises in beautiful stellate groups of flat silky needles, much less soluble than sulphotoluylate of barium; it does not suffer any loss of weight at 150°. The *calcium-salt* of the same acid, $C^{16}H^{18}Ca''S^2O^6$, is very soluble in water, and is obtained by spontaneous evaporation as a shining translucent saline mass.

**PHENYL-ETHYLAMINES.** See Ethyl-aniline, &c., under Phenylamines (p. 450).

**PHENYL-FORMAMIDE** or **FORMANILIDE.** See Formamide (ii. 682).

**PHENYLIC ACID.** Syn. with Phenol.

**PHENYLIDE OF BENZOYL.** Syn. with Phenyl-benzoyl (p. 478).

**PHENYLIDE OF SULPHOPHENYL.** See Sulpho-benzide.

**PHENYL-IMESATINS.** Compounds produced by treating isatin (iii. 406), bromisatin and chlorisatin, dissolved in boiling alcohol, with aniline and its substitution-derivatives. Their relations to imesatin (iii. 246) and their mode of formation are exhibited by the following equations:

$$\underset{\text{Imesatin.}}{C^8H^6N^2O} = \underset{\text{Isatin.}}{C^8H^5NO^2} + NH^3 - H^2O$$

$$\underset{\text{Phenylimesatin.}}{C^{14}H^{10}N^2O} = \underset{\text{Isatin.}}{C^8H^5NO^2} + \underset{\text{Aniline.}}{C^6H^7N} - H^2O$$

$$\underset{\text{Phenyl-bromimesatin.}}{C^{14}H^9BrN^2O} = \underset{\text{Bromisatin.}}{C^8H^4BrNO^2} + \underset{\text{Aniline.}}{C^6H^7N} - H^2O$$

$$\underset{\text{Phenyl-chlorimesatin.}}{C^{14}H^9ClN^2O} = \underset{\text{Chlorisatin.}}{C^8H^4ClNO^2} + \underset{\text{Aniline.}}{C^6H^7N} - H^2O$$

$$\underset{\text{Bromophenyl-imesatin.}}{C^{14}H^9BrN^2O} = \underset{\text{Isatin.}}{C^8H^5NO^2} + \underset{\text{Bromaniline.}}{C^6H^6BrN} - H^2O$$

$$\underset{\text{Chlorophenyl-imesatin.}}{C^{14}H^9ClN^2O} = \underset{\text{Isatin.}}{C^8H^5NO^2} + \underset{\text{Chloraniline.}}{C^6H^6ClN} - H^2O$$

The compounds thus formed crystallise from the alcoholic solution on cooling mostly in yellow or orange-yellow needles. They are insoluble or sparingly soluble in water, easily soluble in hot alcohol. When treated with acids at the boiling heat, they are resolved into isatin, bromisatin or chlorisatin, which is precipitated, and a salt of aniline, chloraniline, or bromaniline which remains in solution. With alkalis they yield a soluble isatate, bromisatate, or chlorisatate, with separation of aniline, bromaniline or chloraniline. Isatin treated with nitraniline or tribromaniline does not yield corresponding compounds (Engelhardt, J. pr. Chem. lxv. 260). See also *Gmelin's Handbook* (xiii. 83).

**PHENYL-ITACONAMIC ACID.**
**PHENYL-ITACONAMIDE.** } See Itaconic Acid (iii. 435).

**PHENYL-MALAMIC ACID.**
**PHENYL-MALAMIIDES.** } See Malic Acid, Phenylated Amides of (iii. 797).

**PHENYL-MERCAPTAN.** See Phenyl, Sulphydrate of (p. 418).

**PHENYL-METHYL.** $C^7H^8 = C^6H^5.CH^3$. (Tollens and Fittig, Ann. Ch. Pharm. cxxxi. 304.)—Produced by the action of sodium on a mixture of bromobenzene and bromide of methyl diluted with pure anhydrous ether, in a vessel externally cooled. The distillate is freed from ether by heating it in the water-bath to 60°, and then rectified two or three times in contact with sodium.

Phenyl-methyl is a transparent colourless liquid, smelling like benzene, having a specific gravity of 0·881 at 5°, and boiling point 111°, which is the same as that assigned by Wilbrand and Beilstein (Ann. Ch. Pharm. cxxviii. 259) to toluene. In fact phenyl-methyl appears to be identical in every respect with toluene obtained from coal-tar (i. 574). It is converted by fuming *nitric acid* into a nitro-compound, $C^7H^7NO^2$, having the peculiar bitter-almond odour of nitrotoluene, boiling at 222°—223° (nitrotoluene boils according to Deville at 225°, according to Wilson at 220°—225°); and converted by sulphide of ammonium into a crystalline base, $C^7H^9N$, having all the properties of ordinary toluidine or benzylamine (i. 575). Phenyl-methyl dissolves in fuming *sulphuric acid*, forming sulphotoluylic acid, $C^7H^8SO^3$; and (like toluene) it is converted by oxidation with *sulphuric acid* and *chromate of potassium* into benzoic acid.

In its identity with toluene, phenyl-methyl differs remarkably from phenyl-ethyl and phenyl-amyl, the former of which is isomeric, but not identical with xylene, the latter with cumene.

**PHENYL-METHYLAMINES.** See Methylaniline, &c., under Phenylamines (p. 453).

**PHENYL-NAPHTHYL-SULPHOCARBAMIDE.** $\left.\begin{matrix}(CS)''\\C^6H^5\\C^{10}H^7\\H^2\end{matrix}\right\}N^2$. Isomeric or identical with sulphocyanate of phenyl-naphthylammonium (see Naphthylamine, p. 22).

**PHENYL-NITROBENZAMIDE.** See Phenyl-benzamide (p. 476).

**PHENYL-OXALURAMIDE.** See Oxaluramide (p. 278).

**PHENYL-OXAMIC ACID.** See Oxamic Ethers (p. 282).

**PHENYL-PHOSPHAMIC ACID.** See Phosphamic Acid.

**PHENYL-PHOSPHAMIDE.** See Phosphamide.

**PHENYL-PHTHALAMIC ACID.**
**PHENYL-PHTHALIMIDE.** } See Phthalic Acid, Amides of.

**PHENYL-PYROTARTRAMIC ACID.**
**PHENYL-PYROTARTRAMIDE.** } See PYROTARTARIC ACID, AMIDES OF.

**PHENYL-SALICYLAMIDE.** See SALICYLAMIDES.

**PHENYL-SINNAMINE.** See SINNAMINE.

**PHENYL-STEARAMIDE.** See STEARIC ACID, AMIDES OF.

**PHENYL-SUBERAMIC ACID.**
**PHENYL-SUBERAMIDE.** } See SUBERIC ACID, AMIDES OF.

**PHENYL-SUCCINAMIC ACID.**
**PHENYL-SUCCINAMIDE.**
**PHENYL-SUCCINIMIDE.** } See SUCCINIC ACID, AMIDES OF.

**PHENYL-SULPHAMIC ACID.** See SULPHAMIC ETHERS.

**PHENYL-SULPHOCARBAMIDES.** See CARBAMIDE (i. 756).

**PHENYL-SULPHOPHENYLAMIDE.** See SULPHOPHENYLAMIDE.

**PHENYL-SULPHURIC ACID.** See SULPHURIC ETHERS.

**PHENYL-SULPHUROUS ACID.** See SULPHUROUS ETHERS.

**PHENYL-TARTRAMIC ACID.**
**PHENYL-TARTRAMIDE.**
**PHENYL-TARTRIMIDE.** } See TARTARIC ACID, AMIDES OF.

**PHENYL-THIOSINAMINE.** See THIOSINAMINE.

**PHENYL-TOLYLAMINE.** See PHENYLAMINES (p. 454).

**PHENYL-UREAS.** See CARBAMIDE (i. 755).

**PHENYL-VALERAMIDE.** See VALERAMIDE.

**PHILLIPSITE.** Lime-harmotome (see HARMOTOME, iii. 13).

**PHILLYGENIN.** $C^{21}H^{24}O^6$. (Bertagnini, Ann. Ch. Pharm. xcvii. 109.)—A resinous substance produced by boiling phillyrin with dilute hydrochloric acid, or better, by the lactic fermentation of phillyrin. It crystallises readily in a white nacreous mass. It is insoluble in cold *water*, very little soluble in boiling water, but dissolves easily in *alcohol* and *ether*. It is polymeric with saligenin: $C^{21}H^{24}O^6 = 3C^7H^8O^2$.

With *chlorine*, *bromine* and *nitric acid*, phillygenin forms substitution-derivatives similar to those obtained in like manner from phillyrin (De Luca). *Monobrophillygenin*, $C^{21}H^{23}BrO^6$, crystallises in shining needles.

**PHILLYRIN.** $C^{27}H^{34}O^{11}$. (Campona, Ann. Ch. Pharm. xxiv. 242.—Bertagnini, *ibid.* xcii. 109.—De Luca, *ibid.* cxviii. 124.)—A substance contained in bark of *Phillyrea latifolia*, whence it is extracted by treating the aqueous decoction of the bark with quick-lime or oxide of lead, evaporating the filtrate, and leaving it to crystallise. According to De Luca, the mother-liquor contains mannite.

Phillyrin is white, crystallisable, inodorous, bitter, sparingly soluble in cold water, more soluble in boiling water and in alcohol (Campona). 1 pt. of phillyrin dissolves at 9° in 1300 pts. water, and in 40 pts. alcohol (De Luca). It is nearly insoluble in ether, quite insoluble in oils both fixed and volatile (Campona). It melts at 160° to a colourless liquid, which begins to decompose at 250°. (De Luca.)

According to Bertagnini, the formula of crystallised phillyrin is $C^{27}H^{34}O^{11}.3\frac{1}{2}H^2O$ (analysis, 57·66—57·88 C and 6·63—6·82 H; calc. 57·75 C, 6·63 H and 35·62 O). The water of crystallisation is given off between 50° and 60°. According to De Luca, the amount of water in phillyrin varies according to the humidity and temperature of the air, and it is all given off at ordinary temperatures over sulphuric acid or in a stream of dry air. Phillyrin melts at about 160° to a colourless mobile liquid. By boiling with dilute *hydrochloric acid*, it is transformed into phillygenin and glucose:

$$\underset{\text{Phillyrin.}}{C^{27}H^{34}O^{11}} + H^2O = \underset{\text{Phillygenin.}}{C^{21}H^{24}O^6} + \underset{\text{Glucose.}}{C^6H^{12}O^6}.$$

It undergoes the same transformation by lactic fermentation. Synaptase has no action upon it. (Bertagnini.)

*Sulphuric acid* first dissolves it with red colour and then decomposes it (Campona). Dilute *nitric acid* forms with it yellow silky crystals; with a less dilute acid, crystalline grains are obtained; with strong boiling nitric acid the products are oxalic acid, and a substance which crystallises in yellow shining laminæ (Bertagnini). According to De Luca, it forms mono- and di-nitro-phillyrin.

*Chlorine* and *bromine* transform phillyrin into substitution-derivatives containing 1 and 2 at. chlorine and bromine, and capable of splitting up, like phillyrin itself, into glucose and chlorinated or brominated derivatives.

**PHLEGMA.** An old name for the watery residue left in the distillation of spirituous or acid liquids.

**PHLEUM.** See GRASSES (i. 943).

**PHLOBAPHENE.** (From φλοιός, bark, and βάφη, colour). A brown substance obtained from the bark of certain trees, *e.g. Pinus sylvestris, Platanus acerifolia, China flava* and *Betula alba.* It is said to have the composition $C^{10}H^{8}O^{4}$, and to form a hydrate containing $\frac{1}{2}$ to $\frac{3}{2}$ at. water. (Hofstetter and Stähelin, Ann. Ch. Pharm. li. 63.—Handw. d. Chem. vi. 226.)

**PHLOGISTON.** See COMBUSTION (i. 1089), and GAS (ii. 774—782).

**PHLOGOPITE.** Rhombic Mica (see MICA, iii. 1012).

**PHLORAMINE.** $C^{6}H^{7}NO^{2} = \left.\begin{matrix}C^{6}H^{5}O^{2}\\H^{2}\end{matrix}\right\}N$. (Hlasiwetz and Pfaundler, Ann. Ch. Pharm. cxix. 202.)—A compound produced by the action of ammonia on phloroglucin:

$$C^{6}H^{6}O^{3} \quad + \quad NH^{3} \quad = \quad C^{6}H^{7}NO^{2} \quad + \quad H^{2}O.$$

Phloroglucin, over which dry ammonia gas is passed, absorbs large quantities of it, and melts; and if, as soon as the formation of water has ceased, the resulting crystalline mass be dissolved in warm water, crystals of phloramine are obtained.—The brown solution of phloroglucin in 5 pts. warm aqueous ammonia, deposits, after standing for some time, crystals which must be purified by recrystallisation from warm water, and dried as quickly as possible in vacuo over oil of vitriol.

Phloramine forms thin, delicate, micaceous laminæ, which separate from the filter in the form of a film having a silky lustre. It has a slightly astringent taste, and is permanent in dry air. It is sparingly soluble in cold *water*, easily soluble in *alcohol*, insoluble in *ether*.

*Decompositions.*—1. Phloramine heated over the water-bath acquires a lemon-yellow and ultimately a dirty brown colour, losing weight at the same time and becoming insoluble in water.—2. Phloramine either moist or dissolved in water turns brown when exposed to the air.—3. *Fuming nitric acid* acts violently on phloramine, producing a yellowish-red solution from which dark brown crystals separate, probably a nitro-compound The same crystals are produced when nitrate of phloramine is kept in the moist state.—4. When phloramine is heated over the water-bath with *oil of vitriol*, a conjugated sulphuric acid is formed, whose barium-salt crystallises in needles. This barium-salt, and the solution obtained by heating phloramine with oil of vitriol, diluting, neutralising with carbonate of barium, boiling and filtering, acquires a fine violet colour on addition of ferric chloride, even if the liquid is very dilute. By *chlorate of potassium and hydrochloric acid*, phloramine is converted into a dark brown resin which gradually becomes lighter in colour, and when distilled, gives off a small quantity of oil having an intensely strong odour (perhaps chlorinated acetone) and leaves a resin. No chloranil is formed in this reaction.—6. When ammoniacal phloroglucin is exposed to the air, the phloramine formed in the first instance disappears, and the liquid dries up to a black shining brittle mass, which dissolves in aqueous ammonia and is thrown down by acids as a black-brown precipitate.—7. By aqueous *alkalis*, phloramine is coloured dark and decomposed.—8. The solution does not colour *ferric chloride* or form a precipitate with *neutral acetate of lead* or *nitrate of silver;* neither does it reduce silver from its solution when heated therewith.

Phloramine unites with acids, forming salts which crystallise well, and are all soluble in alcohol.

*Acetate of Phloramine.*—The solution of phloramine in glacial acetic acid dries up to a yellow varnish without forming crystals. When water is poured upon it, there remains a yellow powder which when heated partly melts to a resin and partly dissolves.

*Hydrochlorate*, $C^{6}H^{7}NO^{2}.HCl$.—Phloramine on which strong hydrochloric acid is poured crumbles to a sandy powder which dissolves when heated, and separates on cooling in yellow shining laminæ, perhaps consisting of the anhydrous salt. After solution in water, white needles and laminæ are slowly obtained, which turn yellow at 100° and give off 10·16 per cent. water (1 at. = 10·02 per cent.).

*Nitrate.*—Phloramine dissolves rapidly in warm moderately concentrated nitric acid, the solution yielding the salt in shining bronze-coloured laminæ and needles.

The *oxalate* is a crystalline salt.

*Sulphate*, $2C^{6}H^{7}NO^{2}.H^{2}SO^{4}$.—A solution of phloramine in dilute sulphuric acid yields by spontaneous evaporation, long yellowish brittle needles, which, when heated over the water-bath, acquire a bright yellow colour and give off 9·38 per cent. water (2 at. = 9·37 per cent.).

**PHLORETAMIC ACID.** $C^9H^{11}NO^2 = \left.\begin{matrix}H^2\\(C^9H^8O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Hlasiwetz, Ann. Ch. Pharm. cii. 162.)—An acid produced by the prolonged action of strong ammonia on ethyl-phloretic acid (p. 491):

$$\left.\begin{matrix}C^2H^5\\(C^9H^8O)''\\H\end{matrix}\right\}O^2 \quad + \quad NH^3 \quad = \quad \left.\begin{matrix}H^2\\(C^9H^8O)''\\H\end{matrix}\right\}N \quad + \quad \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O.$$

After being freed from ammonia and alcohol by evaporation, it crystallises from hot water in slender shining prisms. It dissolves in alcohol and ether, melts between 110° and 111°, and sublimes partially with loss of ammonia. Its aqueous solution is coloured blue by ferric chloride. It appears to unite with alkalis, but does not decompose carbonates, and is altogether but a very feeble acid.

**PHLORETIC ACID.** $C^9H^{10}O^3 = \left.\begin{matrix}(C^9H^8O)''\\H^2\end{matrix}\right\}O^2$. (Hlasiwetz, Wien. akad. Ber. xvii. 382; xxiv. 237; Gm. xiii. 308.)—An acid produced, together with phloroglucin, by the action of caustic potash on phloretin:

$$\underset{\text{Phloretin.}}{C^{15}H^{14}O} \quad + \quad H^2O^5 \quad = \quad \underset{\text{Phloretic acid.}}{C^9H^{10}O^3} \quad + \quad \underset{\text{Phloroglucin.}}{C^6H^6O^3}.$$

It is prepared by dissolving 30 grm. of phloretin in about 200 c. c. of potash-ley of specific gravity 1·25, and evaporating with ebullition till the mass has become thick. The product is then dissolved in boiling water, carbonic acid gas passed through the solution, the liquid evaporated to dryness, and the residue treated with boiling alcohol, which dissolves the phloretate of potassium and leaves the greater part of the phloroglucin undissolved. Ether is then added to the solution, which precipitates the phloretate of potassium as an oily liquid; the ether is decanted; water is added; and the liquid, after concentration, is mixed with hydrochloric acid, which precipitates the phloretic acid: it may be purified by repeated crystallisation from alcohol and from water.

Phloretic acid forms long brittle prisms, having a sour and slightly astringent taste. From alcohol, and especially from ether, it is deposited in very large prisms. The crystals are monoclinic, exhibiting the combination $oP\,.\,\infty P\infty\,.\,-P\infty\,.\,+\frac{4}{3}P\infty\,.\,[P\infty]\,.\,+P$, &c. Angle $-P\infty : \infty P\infty = 138°\,51'$; $+\frac{4}{3}P\infty : \infty P\infty = 143°\,19'$; $[P\infty] : oP = 114°\,15'$. It melts between 128° and 130°, and solidifies in a crystalline mass on cooling. It is somewhat less soluble in *water* than in *alcohol;* the solution may be boiled continuously without decomposition. When mixed with *ammonia* and agitated in the air, it assumes a reddish colour. With solution of *calcic hypochlorite* it assumes a transient brown colour; with *ferric chloride* a green colour. The solution supersaturated with ammonia reduces *nitrate of silver* on application of heat.

*Decompositions.*—1. Phloretic acid when strongly *heated* gives off suffocating odours, burns, and leaves very little charcoal.—2. With *bromine* it forms dibromophloretic acid.—3. Pulverised phloretic acid placed in a flask filled with *chlorine*, melts, with disengagement of heat, the colour of the chlorine disappearing, and hydrochloric acid appearing in its place. The product dissolves in alcohol and in ether, but not in water; the solution when evaporated leaves a soft, sticky mass, which forms with soda a compound solidifying after some time to a deliquescent crystalline mass.—4. With *hydrochloric acid and chlorate of potassium* it assumes at first a reddish-brown colour, gives off abundance of gas when heated, again becomes yellow, and partially changes into yellow flakes.—5. Triturated with *pentachloride of phosphorus*, phloretic acid becomes warm and liquid, and gives off much hydrochloric acid gas with effervescence. On distillation, oxychloride of phosphorus passes over at 100°, and a fuming liquid remains, which decomposes with water, into phloretic acid, hydrochloric acid, and phosphoric acid; and at a higher temperature becomes brown, froths up, and gives off a small quantity of oxychloride of phosphorus, leaving charcoal as a residue.—6. By exposure to the vapour of *sulphuric anhydride*, it is converted into sulpho-phloretic acid, $C^9H^{10}O^3.SO^3$ (Nachbaur, Wien. akad. Ber. xxx. 122).—7. When concentrated *nitric acid* is poured on phloretic acid, it dissolves, forming a red solution, with disengagement of heat, intumescence, and liberation of red vapours; the solution on cooling becomes filled with yellow crystals of dinitrophloretic acid. If the temperature be not kept down, oxalic acid is also formed. Powdered phloretic acid gradually added to cold concentrated nitric acid, is dissolved without formation of red vapours, and after some time dinitrophloretic acid crystallises out. If nitric acid be added to warm aqueous phloretic acid, effervescence takes place, nitric peroxide is disengaged, the liquid becomes coloured, and brown resinous drops separate, which by continued heating with addition of a little nitric acid, disappear, while dinitrophloretic acid crystallises out after a little time.—8. Phloretate of barium mixed with lime, and a little powdered glass, and heated, yields phloretol as a brown oily distillate.

$$C^9H^{10}O^3 \quad + \quad Ba''O \quad = \quad C^8H^{10}O \quad + \quad Ba'CO^3.$$

The same compound is obtained by distilling phloretate of calcium with formate of calcium.—9. With *chloride of acetyl* (or chloride of butyryl or chloride of benzoyl) it gives off hydrochloric acid, and forms peculiar acids (Hlasiwetz). The product formed with chloride of acetyl is acetylphloretic acid, $C^9H^9(C^2H^3O)O^3$ (v. Gilm, Ann. Ch. Pharm. cxii. 180).—10. Phloretate of potassium or phloretate of silver heated with *iodide of ethyl* or *iodide of amyl*, yields ethyl-phloretic acid, $C^9H^9(C^2H^5)O^3$, or amyl-phloretic acid, $C^9H^9(C^5H^{11})O^3$. (Hlasiwetz.)

11. Phloretic acid heated with *phloroglucin* yields, not phloretin but metaphloretin. (Hlasiwetz, p. 492).

PHLORETATES. Phloretic acid is dibasic, forming neutral salts, $C^9H^8M^2O^3$ or $C^9H^8M''O^3$, and acid salts, $C^9H^9MO^3$ or $C^{18}H^{18}M''O^6 = C^9H^8M''O^3.C^9H^{10}O^3$, according to the atomicity of the metal. It decomposes carbonates, mostly forming acid salts. The phloretates are all crystallisable. The acid salts have a neutral, the neutral salts an alkaline reaction. When heated they emit an odour like that of phenol.

*Phloretates of Barium.* The *neutral salt*, $C^9H^8Ba''O^3$, is formed by precipitating a boiling solution of the acid salt with very strong baryta-water. It crystallises from boiling water in needles containing 5 at. water, four of which are given off at 160°. The *acid salt*, $C^{18}H^{18}Ba''O^6$, obtained by saturating a warm aqueous solution of the acid with carbonate of barium, crystallises in long flat transparent prisms, which become dull at 100°.

*Phloretates of Calcium.* The *neutral salt* is precipitated on adding a solution of lime in sugar-water to a concentrated solution of lime in phloretic acid till the liquid becomes alkaline. It crystallises, by evaporation in vacuo, in white laminæ having an alkaline reaction. It is decomposed by carbonic acid.

*Phloretates of Copper.* The *acid salt*, $C^{18}H^{18}Cu''O^6.2H^2O$, obtained by decomposing a solution of the sulphate with phloretate of barium, forms emerald-green crystals which give off their water at 100°, dissolve sparingly in water and alcohol, but readily in ether, with emerald-green colour. The *neutral salt*, $C^9H^8Cu''O^3$, separates out when an ethereal solution of the acid salt is continuously warmed or boiled, in beautiful shining bluish-green spangles containing 1 at. water, half of which is given off at 100°, leaving a hydrate containing $2C^9H^8Cu''O^3.H^2O$.

*Phloretates of Lead.* The *neutral salt*, $2C^9H^8Pb''O^3.H^2O$, is obtained as a heavy bulky precipitate on saturating the acid with carbonate of lead, and mixing the hot filtrate with basic acetate of lead. It retains its water at 100°. A *basic salt* having nearly the composition $2C^9H^8Pb''O^3.Pb''O.2H^2O$, is precipitated on adding basic acetate of lead to a cold solution of phloretic acid saturated with carbonate of lead.

*Phloretate of Magnesium* separates from a solution of magnesic carbonate in aqueous phloretic acid, in colourless crystalline geodes resembling wavellite.

*Phloretates of Mercury.* Phloretic acid forms with *mercurous nitrate* a crystalline precipitate consisting of needles; with neutral *mercuric nitrate* a crystalline precipitate formed of transparent plates.

*Phloretate of Potassium*, $C^9H^9KO^3$, is obtained by mixing the aqueous acid with caustic potash, saturating the liquid with carbonic acid, evaporating, exhausting the dry mass with strong alcohol, and purifying by pressure and recrystallisation. By spontaneous evaporation of the alcoholic solution, it is obtained in colourless radiating laminæ or in rather large prisms. It has a warm saline taste, effloresces in the air, and gives off all its water at 100°. Its alkaline solution turns brown on exposure to the air.

*Phloretate of Silver*, $C^9H^9AgO^3$, is obtained by precipitating the sodium-salt with nitrate of silver. The liquid solidifies to a crystalline magma, which must be filtered in the dark, washed with cold water, and then dried, first between paper, and afterwards at 100°. It forms dazzling white needles, which when moist blacken readily in the light; dissolves easily in ammonia and in acetic acid.

*Phloretate of Sodium*, $C^9H^9NaO^3$, prepared like the potassium-salt, crystallises from a highly concentrated solution, which soon turns reddish in contact with the air, in radiating efflorescent prisms.

*Phloretate of Zinc.*—The *neutral salt* appears to be formed as an insoluble precipieolved,en phloretic acid is boiled with excess of carbonate of zinc, and remains undissolved, while the acid salt passes into solution.

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The *acid salt*, $C^{18}H^{18}Zn''O^6$, crystallises immediately from a solution filtered at the boiling heat, in flat prisms and laminæ of a velvety lustre, and resembling cholesterin; permanent in the air; very sparingly soluble.

*Phloretate of Urea*, $CH^4N^2O.2C^9H^{10}O^3$, is obtained by mixing a solution of 3 pts. of urea and 1 pt. of phloretic acid, in broad, lustrous laminæ, or feathery striated crystals.

### *Derivatives of Phloretic acid.*

**Dibromophloretic acid.** $C^9H^8Br^2O^3$. (Hlasiwetz, Ann. Ch. Pharm. cii. 145.) —Obtained, by adding bromine to pulverised phloretic acid as long as hydrobromic acid continues to escape, as a slightly coloured powder, which crystallises from alcohol in hard colourless prismatic grains, and may be completely purified by washing with water, and precipitation with hydrochloric acid from its solution in ammonia. It melts in an atmosphere of chlorine gas, becoming hot, giving off hydrochloric acid, and forming an uncrystallisable product insoluble in water, soluble in alcohol and ether.

The *ammonium-salt*, $C^9H^7(NH^4)Br^2O^3$, is sparingly soluble in cold water, and easily decomposible. The *barium-salt*, $C^{18}H^{14}Ba''Br^4O^6$ (at 120°), precipitated from the ammonium-salt by chloride of barium, forms prismatic crystals.

**Dinitrophloretic acid.** $C^9H^8N^2O^7 = C^9H^8(NO^2)^2O^3$. (Hlasiwetz, *loc. cit.*) —This compound, produced by the action of nitric acid on phloretic acid, exhibits two different modifications according to the manner in which the action takes place.

The first modification (α) is formed when phloretic acid is dissolved in nitric acid slightly concentrated and kept cool. Yellow grains then form in the red solution; and on recrystallising these from water and alcohol, the acid is obtained in shining lemon-yellow prisms, easily soluble in alcohol with yellowish-red colour, fusible, not detonating, having a slightly bitter taste, and colouring like picric acid.

The detonating salts of this acid are obtained by saturating its aqueous solution with the respective carbonates, or by precipitation from concentrated solutions of the ammonium-salt. The *potassium-salt*, $2C^9H^6K^2(NO^2)^2O^3.H^2O$ (at 120°), crystallises from dilute alcohol in deep orange-coloured prisms. The *barium-salt*, $2C^9H^6Ba''(NO^2)^2O^3.H^2O$, forms orange-coloured needles; the *calcium-salt* yellow needles. The *lead-salt* is a deep red, the *silver-salt* a red, the *copper-salt* a yellow precipitate. The ammonium-salt forms with *mercuric chloride* a yellow precipitate amorphous at first, becoming crystalline afterwards; with *stannous chloride* a yellowish, and with *ferric chloride* a light brown precipitate.

The second modification (β) of the acid is produced by dropping nitric acid into a warm aqueous solution of phloretic acid. The crystals which separate, form when recrystallised from alcohol, dark yellow shining laminæ and scales.

The compounds of this acid with the alkaline earths can be obtained only by saturating the acid with the corresponding hydrates or carbonates, whereas those of the α modification are obtained in the crystalline state by precipitation from the ammonium-salt.

The *β-ammonium-salt*, $2C^9H^6(NH^4)^2(NO^2)^2O^3H^2O$, effloresces in dark yellow needles; the *barium-salt*, $2C^9H^6Ba''(NO^2)^2O^3.H^2O$, separates in nodular groups of orange-yellow crystals.

**PHLORETIC ETHERS.** These are compounds produced by the substitution of 1 at. of an organic radicle for 1 at. hydrogen in phloretic acid.

**Acetic Phloretate** or **Acetyl-phloretic acid.** $C^{11}H^{12}O^4 = C^9H^9(C^2H^3O)O^3$. (H. v. Gilm, Ann. Ch. Pharm. cxii. 180.)—Produced by the action of chloride of acetyl on phloretic acid. When crystallised from dilute alcohol, it forms thin colourless interlaced prisms having a vitreous lustre and an acid reaction. It is insoluble in cold water, soluble in alcohol and ether; melts below the boiling point of water, and partly sublimes; decomposes carbonates; is not coloured by ferric chloride.

*Nitro-acetylphloretic acid*, $C^9H^8(C^2H^3O)(NO^2)O^3$, is obtained by dissolving acetyl-phloretic acid in nitric acid of ordinary strength, and immediately mixing the product with water. It crystallises from alcohol in golden-yellow shining laminæ.

**Ethylic Phloretate** or **Ethyl-phloretic acid.** $C^{11}H^{14}O^3 = C^9H^9(C^2H^5)O^3$. (Hlasiwetz, Ann. Ch. Pharm. cii. 151.)—This compound is easily prepared by heating phloretate of potassium or silver with ethylic iodide to 100° in a sealed tube. It is colourless and viscid; has a faint odour and irritating taste; boils above 265°; is not inflammable; dissolves in alcohol and ether, but is insoluble in water. It has the same index of refraction as salicylic ether for a particular ray in the orange, but its dispersive power is much less than that of salicylic ether.

*Ethylic Dinitrophloretate*, $C^9H^7(C^2H^5)(NO^2)^2O^3$, is obtained by treating ethylic phloretate with nitric acid, as a golden-yellow oil which solidifies in the crystalline form after a while, and crystallises from alcohol in light yellow crystals.

**Amylic Phloretate** or **Amyl-phloretic acid,** $C^{14}H^{20}O^3 = C^9H^9(C^5H^{11})O^3$, prepared like the ethyl-compound, is colourless, very viscid, has a slightly rancid odour, a sharp taste and boils above 290°. With *nitric acid* it yields a crystalline nitro-compound. (Hlasiwetz, *loc. cit.*)

**PHLORETIN.** $C^{15}H^{14}O^5$. (Stas, Ann. Ch. Pharm. xxx. 200.—G. Roser, *ibid.* lxxxiv. 178.—Hlasiwetz, *ibid.* xcvi. 118.—Gm. xvi. 8.)—A substance produced by the action of dilute acids on phlorizin (p. 493). To prepare it, phlorizin is dissolved in a cold dilute acid, and the liquid subsequently heated to 90°: it is then deposited in the crystalline state.

Phloretin crystallises in small white laminæ, having a saccharine taste, nearly insoluble in cold water, very sparingly soluble in boiling water, and in anhydrous ether, soluble in all proportions in boiling alcohol, wood-spirit, and acetic acid, whence it is deposited in shining grains. (Analysis 64·5—65·4 C and 5·2—5·4 H; calc. 65·7 C, 5·1 H, and 29·2 O.)

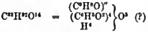
Phloretin melts at 180°, and decomposes at a higher temperature. *Strong acids*, for the most part, dissolve it without alteration. *Nitric acid*, however, converts it into nitro-phloretin. *Chromic acid* resolves it into formic acid and carbonic anhydride (Stas). When pulverised phloretin is treated with *bromine* under ether, a mixture of tri- and tetra-bromophloretin is produced; but when phloretin is heated with excess of bromine, a number of bodies crystallising in needles are formed, which appear to be substitution-products of phloroglucin (Schmidt and Hesse, Ann. Ch. Pharm. cxix. 103). It is dissolved without alteration by *alkalis;* the solutions have a very decided saccharine taste, and in contact with the air, absorb oxygen and form an orange-coloured body. But by boiling and evaporating with strong *potash-ley*, phloretin is resolved into phloretic acid and phloroglucin (pp. 491, 495).

Phloretin rapidly absorbs 13 or 14 per cent. *ammonia-gas*, without losing water. It dissolves in strong aqueous *ammonia*, but separates, after a few seconds, in shining yellow laminæ, which give off ammonia when exposed to the air, or when heated. The solution of the ammoniacal compound precipitates the salts of manganese, iron, zinc, copper, lead, silver, &c. The *lead-compound*, obtained by adding basic acetate of lead to an excess of phloretin-ammonia, and drying the precipitate at 140° in a current of air, contains $2C^{15}H^{14}O^5.5Pb''O$. (Stas.)

*Tetrabromophloretin*, $C^{15}H^{10}Br^4O^5$.—When finely-pulverised phloretin is covered with ether, and bromine added to the mixture cooled from without, the bromine is absorbed, with evolution of heat, and a mixture of tri- and tetra-bromophloretin is formed, which, after removal of the ether and the resulting hydrobromic acid, may be completely converted into tetra-bromophloretin by renewed treatment with bromine at a gentle heat. The product is boiled with water; the residue is dissolved in boiling alcohol; the solution precipitated with water; and the pale yellow crystalline precipitate is purified by boiling with weak alcohol and recrystallisation from boiling alcohol. Phlorizin, treated with bromine under ether, likewise yields tetrabromophloretin, a mixture of mono- and poly-bromophloro-glucin being formed at the same time.

Tetrabromophloretin crystallises in small pale yellow needles, which do not lose weight at 100°; it is decolorised by animal charcoal, but soon turns yellow again. It is insoluble in boiling *water*, sparingly soluble in boiling *alcohol*, easily soluble in *ether*. It melts between 205° and 210°, acquiring a dark red colour, and decomposing with effervescence. It dissolves with yellow colour in aqueous *ammonia* and *soda*, the ammoniacal solution turning brown after a while. In boiling *lime-water* it turns violet, and forms an amorphous violet substance.

*Nitrophloretin*, $C^{15}H^{13}(NO^2)O^5$ (?), called also *phloretic acid* (by Stas), and *nitro-phloretic acid*, is produced by the action of strong nitric acid upon phloretin. It is brown, amorphous, insoluble in water and in dilute acids, soluble in alcohol, wood-spirit, and alkalis. It decomposes at 150°, giving off nitric oxide. Sulphuric acid dissolves it with blood-red colour.



**Metaphloretin.** $C^{33}H^{32}O^{14} = \left.\begin{array}{c}(C^9H^8O)''\\(C^6H^5O^2)^4\\H^4\end{array}\right\}O^5$ (?) (Hlasiwetz, Ann. Ch. Pharm. cxix. 199.)—This compound (not named by Hlasiwetz, but called α-phloretin in *Gmelin's Handbook*, xvi. 10) is produced by heating phloretic acid with phloroglucin. The mixture, heated to 150° in an air-bath, melts together, and gives up water. If kept for six hours between 160° and 180°, it deposits a granular mass, and ultimately becomes quite solid. The brown mass, when boiled with water, dissolves slowly, and the solution, even before it is quite cold, deposits crystalline scales, which may be purified by washing with warm water, and recrystallisation from boiling water with help of animal charcoal.

The compound forms nearly colourless microscopic laminæ, having a rough taste, with sweetish after-taste. It is neutral; unalterable at 150°; colours aqueous *ferric chloride* violet.

**PHLORETOL.** $C^8H^{10}O$.—(Hlasiwetz, Ann. Ch. Pharm. cii. 166.)—This compound, metameric with methylic phenate or phenetol (p. 391), is produced by distilling a mixture of phloretate of barium, caustic lime, and a little powdered glass, in small portions over an open fire. The brown oily distillate is dehydrated by decantation and drying over oil of vitriol, and then rectified.

Phloretol is a colourless, strongly refracting oil, which becomes thicker at 18°, and boils at 190°—200°. Specific gravity 1·0374 at 12°. Vapour-density, obs. = 4·22; calc. = 4·23. It has an aromatic odour, suggestive of phenol, and a burning taste. Placed on the skin it causes a burn. It coagulates albumin almost as rapidly as phenol. A splinter of pine-wood dipped in aqueous phloretol, and then soaked with hydrochloric acid, assumes, when dried in the sun, a colour similar to that of one soaked in phenol. It is only slightly soluble in *water*, but mixes in all proportions with *alcohol* and *ether*.

*Decompositions.*—1. In vessels containing *air*, it becomes yellowish, and then smells of styrol.—2. When soaked up into a wick it may be inflamed, and then burns with a bright, fuliginous flame.—3. Dissolves in *oil of vitriol;* the solution, after standing some time, is no longer precipitated by water, but then contains a conjugated sulphuric acid which forms with baryta a soluble, easily crystallisable salt.—4. When *bromine* is poured on it, hydrobromic acid is liberated, and after the excess of bromine is expelled, a white crystalline substitution-product is left, which is soluble in alcohol, but not in water.—6. With *chlorine* it forms a substitution-product.—7. When dropped into strong *nitric acid* it hisses like a red-hot metal, and forms trinitrophloretol, $C^8H^7(NO^2)^3O$, with violent action and disengagement of nitric peroxide.

**PHLORETYL.** $C^9H^8O$.—The hypothetical diatomic radicle of phloretic acid and its derivatives.

*Chloride of phloretyl*, $(C^9H^8O)''Cl^2$, appears to be formed by the action of pentachloride of phosphorus on phloretic acid, according to the equation,

$$3\left[\left.\begin{matrix}(C^9H^8O)''\\H^2\end{matrix}\right\}O^3\right] + 3PCl^5 = 3C^9H^8OCl^2 + 2POCl^3 + 3HCl + PH^3O^4.$$

On distilling the product, oxychloride of phosphorus passes over at 110°, and the residue can no longer be heated without decomposition. When treated with water, however, it yields phloretic, phosphoric, and hydrochloric acids. (Hlasiwetz.)

**PHLORIZEIN.** $C^{21}H^{30}N^2O^{13}$. (Stas, Ann. Ch. Pharm. xxx. 206.)—Produced by the simultaneous action of air and ammonia on phlorizin:

$$C^{21}H^{24}O^{10} + 2NH^3 + O^3 = C^{21}H^{30}N^2O^{13}.$$

It is precipitated on adding an acid to the product of the reaction. To obtain it pure, Stas (Ann. Ch. Phys. lxix. 367) precipitates the crude product of the above reaction with alcohol; dissolves the precipitate in the smallest possible quantity of water; and adds alcohol acidulated with acetic acid to the solution drop by drop. The precipitate is then washed with alcohol of continually increased strength.

Phlorizein is a reddish-brown, uncrystallisable solid, differing in aspect according to the state in which it is examined. Its taste is slightly bitter. It dissolves easily in boiling water, but is nearly insoluble in alcohol, ether, and wood-spirit. It yields by analysis 48·1—48·5 C, 5·6—5·4 H and 5·0—5·4 N: (calc. 48·6 C, 5·8 H, 5·4 N, and 40·2 O).

Phlorizein is decomposed by heat. Fixed alkalis gradually alter its colour, transforming it into a brownish substance.

*Phlorizeate of ammonium* is difficult to obtain pure. The best mode of preparation is to place phlorizin under a bell-jar above a solution of carbonate of ammonia, into which fragments of caustic potash are thrown from time to time. If care be taken to avoid an excess of ammonia, a blue crystallisable substance very soluble in water is sometimes obtained; but more frequently the product is brown-red.

The compound is decolorised by sulphydric acid, sulphide of ammonium, and stannate of potassium, but the decolorised solution gradually resumes its blue tint on exposure to the air. The solution of phlorizeate of ammonium is likewise decolorised by hydrate of aluminium, the alumina acquiring a blue colour.

The solution precipitates salts of iron, zinc, lead, and silver. The silver-precipitate is blue, and is decomposed by water.

**PHLORIZIN.** $C^{21}H^{24}O^{10}$.—*Phlorrhizin*, *Phloridzin* (from φλοιός, bark, and ῥίζα, root). [Stas and De Koninck (1835), Ann. Ch. Pharm. xv. 75.—Stas, Ann. Ch. Phys. [2] lxix. 367.—Mulder, Rev. Scient. iii. 50.—Roser, Ann. Ch. Pharm. lxxxiv. 178.—Strecker, *ibid.* lxxiv. 184.—Gm. xvi. 11.]—A substance existing ready formed in the root-bark of the apple, pear, plum, and cherry-tree. It is extracted by weak alcohol, and the alcoholic solution, decolorised by animal charcoal, and concentrated, deposits crystals of phlorizin on cooling. The root-bark of the apple-tree is the best source of phlorizin, because it contains less colouring matter than that of the other trees.

Phlorizin crystallises in long silky needles or tufts. It has a slightly bitter taste, is sparingly soluble in cold water, but dissolves in all proportions in boiling water. *Alcohol* and *wood-spirit* dissolve it readily, but it is quite insoluble in *ether*.

The crystals of phlorizin contain 2 at. water, $C^{21}H^{24}O^{10}.2H^2O$ (analysis, 52·8—53 9 C and 6·0—62 H; calc. 53·4 C, 5·9 H, and 40·7 O). At 100° they give off their water (7·6 per cent.) and leave anhydrous phlorizin, $C^{21}H^{24}O^{10}$ (anal. 57·4 C and 5·7 H; calc. 57·8 C and 5·5 H), which melts at 109° and decomposes at 200° yielding a red substance called rufin and other products.

Strong *sulphuric acid* at 60° or 70° converts it into a red substance called rufi- or rutilo-sulphuric acid. (Mulder.)

By prolonged contact with dilute *sulphuric*, *phosphoric*, or *hydrochloric acid* it is resolved into glucose and phloretin. The same change is induced by *oxalic acid* at 90°:

$$\underset{\text{Phlorizin.}}{C^{21}H^{24}O^{10}} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\text{Phloretin.}}{C^{15}H^{14}O^5}.$$

100 pts. of phlorizin thus treated yield from 41 to 42 pts. glucose (calc. 41·3 pts.).

Strong *nitric acid* converts it into oxalic acid and nitrophloretin, $C^{15}H^{13}(NO^2)O^5$(?)

Strong *hydrochloric acid* converts phlorizin into a dirty red, amorphous substance without dissolving it. (De Koninck.)

When phlorizin is triturated with $\frac{1}{10}$ of its weight of *iodine*, a greyish-violet mass is formed, from which water separates black flocks (Vogel, N. Br. Arch. xvi. 155).—When phlorizin is covered with ether and *bromine* is dropped into the liquid, as long as it is decolorised thereby, the phlorizin dissolves completely; and on evaporating the solution, boiling the residue with dilute sulphuric acid (to decompose phlorizin), and recrystallising, tetrabromophloretin (p. 492) is obtained (Schmidt and Hesse, Ann. Ch. Pharm. cxix. 105).—*Chlorine*, *bromine* and *iodine* evolve heat from dry phlorizin, and convert it into a brown viscid resin (De Koninck). Phlorizin treated with *chloride of iodine* yields only amorphous products (Stenhouse, Ann. Ch. Pharm. cxxxiv. 218).

Alkalis dissolve phlorizin without alteration, and the solutions are permanent in the air. Boiling potash produces a black substance.

Phlorizin absorbs 11 or 12 per cent. of dry *ammonia-gas*, and the product exposed to the air gradually assumes an orange then a red tint, ultimately becoming dark blue, and then consists of phlorizeate of ammonium (p. 493).

*Phlorizate of Barium* is obtained by mixing the solutions of phlorizin and baryta in wood-spirit. A precipitate is then formed which loses its alkaline reaction on exposure to the air, and becomes brownish-red, yielding carbonic anhydride, acetic acid, and a peculiar colouring matter. It appears to contain $C^{21}H^{24}O^{10}.Ba''O$. (anal. 40·3 C, 4·1 H, and 29·8—30·2 BaO; calc. 42·8 C, 4·1 H, and 25·8 BaO).

*Phlorizate of Calcium* appears to contain $2C^{21}H^{24}O^{10}.3Ca''H^2O^2$ (anal. 15·2—14 per cent. lime; calc. 15·3.) It is obtained by evaporating a solution of phlorizin or lime-water. By exposure to the air, it is decomposed like the barium-compound.

*Phlorizate of Lead* appears to contain $C^{21}H^{24}O^{10}.3Pb''O$ (anal. 24·9 C, 2·1 H, and 59·2—60·0 PbO; calc. 22·7 C, 2·1 H and 60·6 PbO). It is produced as a white precipitate on adding basic acetate of lead to a boiling solution of phlorizin, the latter being in excess.

**PHLOROGLUCIN.** $C^6H^6O^3$. (Hlasiwetz, Ann. Ch. Pharm. xcvi. 118; cxii. 96; cxix. 199.—Gm. xv. 65.)

*Formation.*—1. Phloretin boiled with potash-ley is resolved into phloretic acid and phloroglucin.—2. Quercetin, under the same circumstances, is resolved into quercetic acid and phloroglucin. According to Hlasiwetz:

$$\underset{\text{Quercetin.}}{C^{23}H^{16}O^{10}} + H^2O = \underset{\substack{\text{Quercetic}\\\text{acid.}}}{C^{17}H^{12}O^8} + \underset{\text{Phloroglucin.}}{C^6H^6O^3};$$

according to Zwenger and Dronke (Ann. Ch. Pharm. cxxiii. 154):

$$\underset{\text{Quercetin.}}{3C^{13}H^{10}O^6} + H^2O = \underset{\substack{\text{Quercetic}\\\text{acid.}}}{C^{21}H^{14}O^{10}} + \underset{\substack{\text{Phloro-}\\\text{glucin.}}}{3C^6H^6O^3}.$$

3. Quercetin in alkaline solution treated with sodium-amalgam is also converted into phloroglucin, together with a colourless product different from quercetic acid

(Hlasiwetz, Ann. Ch. Pharm. cxxiv. 358).—4. Morintannic acid or maclurin (iii. 1049), mixed with hydrate of potassium and evaporated to a pasty mass, is resolved into phloroglucin and protocatechuic acid (Hlasiwetz and Pfaundler):

$$\underset{\text{Morintannic acid.}}{C^{13}H^{10}O^{6}} + H^{2}O = \underset{\text{Phloroglucin.}}{C^{6}H^{6}O^{3}} + \underset{\text{Protocatechuic acid.}}{C^{7}H^{6}O^{4}}.$$

*Preparation.*—1. The mixture of phloroglucin and carbonate of potassium obtained as described in the preparation of phloretic acid (p. 489) from which all the phloretate of potassium has been extracted by alcohol, is dissolved in water; dilute sulphuric acid is added in slight excess; and the mass is evaporated to dryness over the water-bath, and then well boiled with alcohol (better with ether-alcohol). The alcohol is distilled off and the residue left to crystallise, whereby strongly coloured crystals are obtained, the mother-liquor also yielding an additional quantity. They are dissolved in water, and the solution is mixed with acetate of lead (which produces no precipitate), and saturated with sulphydric acid, the precipitated sulphide of lead carrying down nearly the whole of the colouring matter, so that the crystals which afterwards separate have only a yellowish tint. By re-crystallisation from ether and afterwards from water, they may be obtained quite colourless.

2. Quercetin is added to a hot concentrated solution of 3 pts. hydrate of potassium, the liquid evaporated down at the boiling heat, and the residue further heated, till a sample of it taken out no longer yields a flocculent precipitate with hydrochloric acid, but quickly assumes a deep red colour when dissolved in water. The whole is then immediately dissolved in water; the solution, which instantly turns red, is neutralised with hydrochloric acid; and the flocks (of alpha-quercetin and undecomposed quercetin) which are deposited from the liquid on standing and cooling, are separated by filtration. The filtrate is evaporated to dryness, the residue exhausted with alcohol; the alcohol distilled off from the brown tincture; the residue dissolved in water, and mixed with acetate of lead, whereby quercetate of lead is precipitated, while phloroglucin remains in solution. The latter is obtained in the crystalline state by removing the lead from the filtrate with sulphydric acid and quickly evaporating, and is purified by re-crystallisation, with help of animal charcoal.

*Properties.*—Phloroglucin separates from aqueous solution in hydrated crystals $C^{6}H^{6}O^{3}.2H^{2}O$, belonging to the trimetric system; by slow evaporation they may be obtained of the size of peas, and with irregular prismatic faces. The crystals grate between the teeth, effloresce in warm air and in vacuo, or more quickly at 90°, giving off 22·25 to 22·47 per cent. water (2 at. = 22·2 per cent.), and leaving anhydrous phloroglucin. The anhydrous compound also separates directly from solution in anhydrous ether. Phloroglucin is sweeter than common sugar, neutral to vegetable colours, permanent in the air at ordinary temperatures, melts at about 220°, sublimes without particular odour and solidifies on cooling. It dissolves in *water* and *alcohol*, and readily in *ether*. It is not altered by *hydrochloric acid;* does not precipitate any metallic salt except *basic acetate of lead* with which it forms the compound $C^{6}H^{6}O^{3}.2Pb''O$. It is coloured deep violet-red by *ferric chloride*, and produces with *chloride of lime*, a reddish-yellow colour which however soon disappears. It forms a compound with *potash*, which gradually separates in red-brown drops from the alcoholic extract of the product obtained by boiling phloretin with potash.

*Decompositions.*—Ammoniacal phloroglucin shaken up with air, becomes red-brown and afterwards opaque. Phloroglucin in concentrated aqueous solution is converted by *bromine* into tribromo-phloroglucin, which immediately separates in the crystalline form, the liquid becoming hot, and emitting a highly tear-exciting odour. *Nitric acid* dissolves it with brown colour, and converts it into nitrophloroglucin (p. 496).—*Ammonia* converts it into phloramine, $C^{6}H^{7}NO^{2}$ (p. 488). It reduces an *alkaline solution of cupric oxide*, like grape-sugar. It reduces *mercurous nitrate* when heated with it, and likewise *nitrate of silver*, with peculiar quickness on addition of ammonia. With *chloride of acetyl, chloride of benzoyl*, &c., it forms substitution-products, p. 496).

### *Derivatives of Phloroglucin.*

**Tribromophloroglucin.** $C^{6}H^{3}Br^{3}O^{3}$. (Hlasiwetz, Ann. Ch. Pharm. xcvi. 118.)—Produced by dropping bromine into concentrated aqueous phloroglucin till the colour of the bromine is no longer destroyed, and the liquid has solidified to a crystalline pulp; the product is then collected on a filter, washed with cold water, and recrystallised from boiling water with help of animal charcoal.

It crystallises from water in long needles (mostly brownish), from alcohol in concentrically united prisms, containing $C^{6}H^{3}Br^{3}O^{3}.3H^{2}O$, which give off their water in warm air, or at 100°, and are reduced to anhydrous tribromophloroglucin. The compound dissolves very slightly in cold, more freely in boiling *water*, but appears to be partly decomposed by continued boiling. It dissolves very readily in alcohol, and with brown colour in aqueous alkalis and alkaline carbonates.

**Nitrophloroglucin.** $C^6H^5NO^5 = C^6H^4(NO^2)O^3$. (Hlasiwetz and Pfaundler, Ann. Ch. Pharm. cxix. 199.)—When phloroglucin is added by small quantities to somewhat dilute nitric acid moderately heated and kept at a uniform temperature, a deep red solution is formed, which deposits the nitro-compound in small nodules: by recrystallisation from hot water it may be obtained in reddish-yellow shining scales and laminæ, having a slightly bitter taste. It is slightly soluble in water, forming a yellow solution.

**Acetyl-phloroglucin.** $C^{12}H^{12}O^6 = C^6H^3(C^2H^3O)^3O^3$? (Hlasiwetz and Pfaundler, Ann. Ch. Pharm. cxix. 201.)—Chloride of acetyl acts on phloroglucin even at mean temperatures, and at higher temperatures converts it, with evolution of hydrochloric acid, into a white crystalline mass of the acetyl-compound which, after the excess of chloride of acetyl has been expelled, may be recrystallised from alcohol. It forms small colourless prisms which give off acetic acid when heated, and are insoluble in water. Its rational formula is deduced from the analogy of benzoylphloroglucin, analysis giving no means of determining whether 1, 2, or 3 at. acetyl have entered into the phloroglucin in place of hydrogen, inasmuch as all three products would have the same per-centage composition. (Hlasiwetz.)

**Benzoyl-phloroglucin.** $C^{27}H^{18}O^6 = C^6H^3(C^7H^5O)^3O^3$. (Hlasiwetz and Pfaundler, *loc. cit.*)—Produced by the action of chlorido of benzoyl on phloroglucin, and purified by boiling with alcohol, in which it is nearly insoluble. Crystallises in small, white, shining scales.

**PHLORONE.** $C^8H^8O^2$. (Rommier and Bouilhon, Compt. rend. lv. 214.)—This compound, homologous with quinone ($C^6H^4O^2$), is produced by distilling 2 pts. of coal-tar creosote (the portion of crude carbolic acid boiling between 195° and 220°), and 3 pts. oil of vitriol in a capacious retort, adding chromate of potassium (or better, peroxide of manganese) from time to time. A yellow distillate is thus obtained mixed with yellow drops which quickly solidify, and may be purified by pressure between paper and recrystallisation from water at 60°. It forms splendid yellow flexible needles, soluble in alcohol, only slightly soluble in cold water, and smelling like quinone. It melts at 60°—62°, and volatilises with vapour of water, part of it however being blackened and decomposed at the same time.

The solution of phlorone, like that of quinone, is turned brown by alkalis, and then yields a brown flocculent precipitate with acids. Phlorone is decolorised and reduced by *sulphurous acid*, yielding a very soluble crystalline body, probably homologous with hydroquinone; it does not act on polarised light.

Metaphlorone. This is a less soluble isomeric modification of phlorone, which remains behind when phlorone is dissolved in water at 60°, but crystallises in small needles from water at 90°. It melts at 125°, dissolves in hot water somewhat more readily than in cold, and behaves to acids and alkalis like phlorone.

**PHOCENIC ACID.** Syn. with DELPHINIC ACID (ii. 309).

**PHOCENIL** or **PHOCENIN.** Syn. with DELPHIN (ii. 309).

**PHŒNICIN.** Syn. with SULPHOPHŒNICIC ACID. See INDIGO-SULPHURIC ACIDS (iii. 261).

**PHŒNICITE** or **PHŒNIKOCHROÏTE.** Syn. with MELONACHROÏTE (iii. 866).

**PHOLERITE.** A kind of clay, not differing much from Kaolin in composition, but occurring in soft, white nacreous scales. Specific gravity 2·35—2·57. Infusible. Occurs at Fins in the dept. of Allier, and at Rive de Gier, dept. de la Loire, France, filling fissures in nodules of iron ore in the coal formation; also at Cache-Après, at Mons in Belgium; with emery at Naxos, and with diaspore at Schemnitz (Dana); in fissures of the bluish-grey sandstone of Lodère in Hérault (Pisani) near Freiberg, &c. (R. Müller, Jahresb. 1861, p. 1003.)

**PHONOLITE.** Syn. with CLINKSTONE (i. 1025).

**PHORMINE** or *Pseudomorphine*. See MORPHINE (iii. 1051).

**PHORONE.** Syn. with CAMPHORONE (i. 733).

**PHOSGENE.** Syn. with OXYCHLORIDE OF CARBON or CHLORIDE OF CARBONYL (i. 774).

**PHOSGENITE.** Chlorocarbonate of Lead (iii. 339).

**PHOSPHACETIC ACID.** One of the acids which Zeise obtained by the action of phosphorus on acetone (i. 28).

**PHOSPHAM.** $PHN^2$. (H. Rose, Pogg. Ann. xxviii. 529.—Gerhardt, Ann. Ch. Phys. [3] xviii. 188.—Schiff, Ch. Pharm. ciii. 188.)—This compound is the nitrile of phosphoric acid, its relation to that acid being similar to that of acetonitrile to acetic acid:

$$\underset{\text{Acetic acid.}}{C^2H^4O^2} + NH^3 - 2H^2O = \underset{\text{Acetonitrile.}}{C^2H^3N.}$$
$$\underset{\text{Phosphoric acid.}}{PH^3O^4} + 2NH^3 - 4H^2O = PHN^2.$$

It is obtained: 1. By passing ammonia-gas over pentachloride of phosphorus, and heating the product in a stream of carbonic anhydride (H. Rose). According to Rose the compound thus formed is a dinitride of phosphorus, $PN^2$; but according to Gerhardt it has the composition above given, its formation taking place as shown by the equation:

$$PCl^5 + 2NH^3 = 5HCl + PHN^2.$$

2. By saturating phosphoric anhydride as completely as possible with ammonia-gas, and heating the product in a dry current of that gas (Schiff):

$$P^2O^5 + 4NH^3 = 2PHN^2 + 5H^2O.$$

On treating the product with cold water, phosphoric acid dissolves, and phospham remains.

Phospham, prepared by the first process, is a bulky powder, white if moisture has been carefully excluded during its preparation, reddish in the contrary case; as obtained by the second process it is yellowish-red. When heated in a close vessel it neither fuses nor volatilises. Water decomposes it at a high temperature, forming ammonia and phosphoric acid, and it is decomposed in like manner by fusion with hydrate of potassium.

**PHOSPHAMIC ACID.** $PH^2NO^2 = \left.\begin{matrix}H\\(PO)'''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—This compound is produced, according to Schiff (Ann. Ch. Pharm. ciii. 168), by the action of ammonia-gas on phosphoric anhydride, according to the equation:

$$P^2O^5 + 2NH^3 = 2PH^2NO^2 + H^2O,$$

also by the action of water on chloronitride of phosphorus:

$$NPCl^2 + 2H^2O = PH^2NO^2 + 2HCl.$$

Gladstone, however (Chem. Soc. J. xvii. 229), has shown that the product formed in both these reactions is pyrophosphodiamic acid, $P^2N^2H^6O^5 = \left.\begin{matrix}H^4\\(P^2O^3)^{iv}\\H^2\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix}$, according to the equations:

$$P^2O^5 + 2NH^3 = P^2N^2H^6O^5.$$
$$2N^3P^3Cl^6 + 15H^2O = 3P^2N^2H^6O^5 + 12HCl.$$

(See PYROPHOSPHAMIC ACIDS.)

*Phenyl-phosphamic acid*, $\left.\begin{matrix}C^6H^5\\(PO)'''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—Aniline acts strongly on phosphoric anhydride, apparently producing this compound (Schiff) [or perhaps phenyl-pyrophosphodiamic acid].

**PHOSPHAMIDES.** These are compounds formed from one or more molecules of ammonia, by the substitution of phosphatyl, PO, for 3 atoms of hydrogen. (Gerhardt, Ann. Ch. Phys. [3] xviii. 188.—H. Schiff, Ann. Ch. Pharm. ci. 300.)

1. *Phosphomonamide*, $N(PO)'''$. (Gerhardt's *Biphosphamide*.)—This compound, which contains the elements of mono-ammonic phosphate *minus* 3 at. water $[PH^2(NH^4)O^4 - 3H^2O]$, is obtained by heating phosphodiamide or phosphotriamide without access of air:

$$\underset{\text{Phosphodiamide.}}{N^2H^3PO} - NH^3 = NPO.$$
$$\underset{\text{Phospho-triamide.}}{N^3H^6PO} - 2NH^3 = NPO.$$

It is a pulverulent substance resembling phospho-triamide in its reactions, but still more difficult to decompose.

2. *Phosphodiamide*, $\left.\begin{matrix}(PO)'''\\H^3\end{matrix}\right\}N^2$. (Gerhardt's *Phosphamide*.)—This amide which may be regarded as diammonic phosphate, $PH(NH^4)^2O^4$, *minus* 3 at. water, is produced: 1. By saturating pentachloride of phosphorus with ammonia-gas, whereby the so-called

*chlorophosphamide*, $N^2H^4PCl^3$, appears to be first formed,* and boiling this product with water:

$$\begin{array}{llllllll} & PCl^5 & + & 4NH^3 & = & N^2H^4PCl^3 & + & 2NH^4Cl. \\ \text{and} & N^2H^4PCl^3 & + & H^2O & = & N^2H^3PO & + & 3HCl. \end{array}$$

The product is purified by boiling, first with caustic potash, then with nitric or sulphuric acid, and finally, by washing with water. It is a white powder, insoluble in water, alcohol, and oil of turpentine. When heated without access of air, it gives off ammonia, and leaves phosphomonamide; but if moisture be present, it yields ammonia and metaphosphoric acid. Fused with hydrate of potassium, it gives off ammonia and leaves phosphate of potassium. It resists the action of most oxidising agents; but is slowly oxidised by fusion with nitre, and deflagrates with chlorate of potassium.

Liebig and Wöhler, who discovered this compound, supposed it to be a hydrate of phosphide of nitrogen, $PN^2.H^2O$.

3. *Phosphotriamide*, $\left.\begin{matrix}(PO)''' \\ H^6\end{matrix}\right\}N^3 = P(NH^4)^3O^4 - 3H^2O$.—When dry ammoniacal gas is slowly passed into oxychloride of phosphorus (chloride of phosphatyl, $POCl^3$), and the product afterwards treated with water, a solution of sal-ammoniac is obtained, together with a snow-white, amorphous insoluble substance, which is phosphotriamide:

$$POCl^3 + 6NH^3 = 3NH^4Cl + N^3H^6PO.$$

This compound is scarcely attacked by continued boiling with water, potash-ley, or dilute acids. It is very slowly decomposed by boiling with strong nitric or hydrochloric acid, more readily by aqua-regia. Strong sulphuric or nitro-sulphuric acid dissolves it easily at a gentle heat, forming a solution which contains ammonia and phosphoric acid. It is not completely decomposed by heating with soda-lime. When fused with hydrate of potassium, it gives off a large quantity of ammonia, and leaves phosphate of potassium. Heated alone, out of contact of air, it also gives off ammonia, and leaves phosphomonamide, which, on being heated with potash, evolves more ammonia, and leaves phosphate of potassium.

*Triphenyl-phosphotriamide*, $\left.\begin{matrix}(PO)''' \\ (C^6H^5)^3 \\ H^3\end{matrix}\right\}N^3$, is obtained by the action of anhydrous aniline on oxychloride of phosphorus; it is a white mass, more easily decomposible than phosphotriamide.

*Trinaphthyl-phosphotriamide*, $\left.\begin{matrix}(PO)''' \\ (C^{10}H^7)^3 \\ H^3\end{matrix}\right\}N^3$, is obtained in like manner by the action of naphthylamine, $(C^{10}H^7)H^2N$, on oxychloride of phosphorus.

*Sulphophosphotriamide*, $\left.\begin{matrix}(PS)''' \\ H^6\end{matrix}\right\}N^3$, is obtained by treating sulphochloride of phosphorus, $PSCl^3$, with ammoniacal gas; it is also a white mass, which is decomposed by water, with evolution of sulphydric acid gas.

*Triphenyl-sulphophosphotriamide*, $\left.\begin{matrix}(PS)''' \\ (C^6H^5)^3 \\ H^3\end{matrix}\right\}N^3$; is obtained in like manner, by the action of aniline on sulphochloride of phosphorus. (Schiff, Ann. Ch. Pharm. ci. 300.)

**PHOSPHAMMONIUMS.** Bases formed on the mixed type, $\left.\begin{matrix}mH^4N \\ nH^4P\end{matrix}\right\}$; for example, *ethylene-trimethyl-triethyl-phosphammonium*, $\left.\begin{matrix}(C^2H^4)'' \\ (CH^3)^3 \\ (C^2H^5)^3\end{matrix}\right\}\begin{matrix}N \\ P.\end{matrix}$

**PHOSPHAMYL-TRIETHYLIUM** and **PHOSPHAMYL-TRIMETHYLIUM.** (See PHOSPHORUS-BASES.)

**PHOSPHANILIC ACID.** Syn. with PHENYL-PHOSPHAMIC ACID (p. 498).

**PHOSPHANTIMONIC ACID.** This name is applied to the solution obtained by dropping pentachloride of antimony into aqueous phosphoric acid. It precipitates certain alkaloïds, morphine, narcotine, nicotine, &c.

**PHOSPHARSONIUMS.** Bases formed on the mixed type, $\left.\begin{matrix}mH^4P \\ nH^4As\end{matrix}\right\}$, *e.g. ethylene-hexethyl-phospharsonium*, $\left.\begin{matrix}(C^2H^4)'' \\ (C^2H^5)^6\end{matrix}\right\}\begin{matrix}P \\ As.\end{matrix}$

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* The action of ammonia on pentachloride of phosphorus is complicated, several products being formed, one of which is chloronitride of phosphorus, $P^3N^3Cl^6$.

**PHOSPHATES.** See Phosphorus, Oxides and Oxygen-acids of.

**PHOSPHATIC ACID.** *Hypophosphoric acid. Pelletier's Phosphorous acid.*—These names are applied to the syrupy mixture of phosphoric and phosphorous acids produced by the slow combustion of phosphorus in moist air. A convenient way of preparing it is to introduce a number of separate sticks of phosphorus into glass tubes an inch long, open above and below, but drawn out funnel-shape at the bottom, these tubes being arranged in a funnel, and the funnel inserted into a bottle which stands in a dish containing water. The whole arrangement is covered with a bell-jar, but in such a manner as to give access to the external air, which however should not be very warm as in that case the phosphorus may melt and take fire. The acid which collects in the bottle is equal to three times the weight of the phosphorus consumed, but may be obtained in a more concentrated state by evaporation. It is a mixture of about 1 at. phosphorous acid to 4 at. phosphoric acid.

**PHOSPHETHIC ACID.** The name given by Zeise (Ann. Ch. Pharm. xli. 31) to an acid which he obtained by the action of finely divided phosphorus on ether.

**PHOSPHETHYLIUM.**
**PHOSPHETHYL-TRIMETHYLIUM.** } See Phosphorus-bases.

**PHOSPHIDES.** Compounds of phosphorus with more basic elements or compound-radicles. The phosphides of hydrogen have been already described (iii. 199); also the general characters of the metallic phosphides (iii. 941); for the special descriptions, see the several metals. The phosphides of the alcohol-radicles, *e.g.* triethyl-phosphine $(C^2H^5)^3P$, will be described under Phosphorus-bases.

**PHOSPHITES.** See Phosphorus, Oxygen-acids of.

**PHOSPHO-BENZAMIC ACID.** An acid produced by the action of phosphoric anhydride on oil of bergamot (i. 581).

**PHOSPHOCERITE.** Native phosphate of cerium. (See Phosphates.)

**PHOSPHOCHALCITE.** Native hydrated cupric phosphate. (See Phosphates.)

**PHOSPHOGLYCERIC ACID.** Syn. with Glycerophosphoric Acid (ii. 891).

**PHOSPHO-HYDROQUINONIC ACID.** $C^6H^7PO^5$. (See Derivatives of Hydroquinone, iii. 217.)

**PHOSPHO-METHYLIUM.**
**PHOSPHOMETHYL-TRIETHYLIUM.** } See Phosphorus-bases.

**PHOSPHOMOLYBDIC ACID.** See Molybdenum (iii. 1037).

**PHOSPHORESCENCE.** See Light (iii. 590, 632.)

**PHOSPHORIC ACID.**
**PHOSPHORIC ETHERS.** } See Phosphorus, Oxygen-acids of.

**PHOSPHORITE.** A massive radiated variety of apatite (i. 348), chiefly obtained from Estremadura in Spain and Schlackenwald in Bohemia.

**PHOSPHOROCHALCITE.** A variety of hydrated cupric phosphate. (See Phosphates.)

**PHOSPHOROSAMIDES.** Amides in which 3 at. hydrogen are replaced by 1 at. phosphorus. Trichloride of phosphorus absorbs 3 at. of ammonia, forming a white mass of sal-ammoniac and phosphoroso-triamide, $N^3H^6P'''$:

$$PCl^3 + 6NH^3 = 3NH^4Cl + N^3H^6P.$$

This mass when heated out of contact with the air, gives off ammonia and sal-ammoniac, leaving a yellowish amorphous residue which has been described as a phosphide of nitrogen, but which in all probability is a mixture of phosphoroso-diamide, $N^2H^3P'''$, and phosphoroso-monamide, $NP'''$.

**PHOSPHOROUS ACID AND ETHERS.** See Phosphorus, Oxygen-acids of.

**PHOSPHORUS.** *Atomic weight* 31. *Symbol* P. *Combining volume* ½. *Vapour-density*, by calculation = 62 referred to hydrogen as unity; 4·284 referred to air; by observation, 62·1 and 4·35.

This element, though very widely diffused in water, is never found in the uncombined state, but almost always in the form of a metallic phosphate, and chiefly as phosphate of calcium, which forms the principal constituent of apatite, phosphorite, coprolites, &c. Combined phosphoric acid is also found, though in very minute proportions, in most of the primitive rocks, and in soils produced by their disintegration, whence it is taken up by plants, accumulating chiefly in the seed. From the vegetable it passes into the

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animal kingdom, where it exists in the largest proportion. It is found in the blood, in the urine, in all the soft tissues, especially the nervous tissue, and in the bones, of which indeed phosphate of calcium constitutes the chief earthy constituent. Traces of phosphoric acid have also been found in the water of springs and rivers, and according to Barral (Compt. rend. li. 769) in rain-water.

Phosphorus was discovered in 1669 by Brandt of Hamburg, who obtained it by distilling the residue of evaporated urine with charcoal. Gahn in 1769 showed it to be a constituent of bones, and Scheele, six years later, founded on this observation a process for the extraction of phosphorus from bones, namely by digesting white-burnt bones for several days with dilute nitric acid, removing the lime by sulphuric acid, evaporating to a syrup, and distilling with charcoal powder. This process was simplified by Nicolas and Polletier (J. Phys. xi. and xxviii.) who decomposed the bone-ash directly with sulphuric acid; and Fourcroy and Vauquelin (J. Pharm. i. 9) afterwards determined the exact proportion of sulphuric acid required for the complete decomposition of the bone-earth.

Bone-earth consists mainly of tricalcic phosphate $\overset{\prime\prime}{\mathrm{Ca}}{}^3\mathrm{P}^2\mathrm{O}^8$. Now earthy and alkaline phosphates containing 3 atoms of metal are not decomposed by ignition with charcoal, but phosphoric acid and anhydride are completely reduced by this treatment, while the metaphosphates, which may be regarded as compounds of trimetallic phosphates with phosphoric anhydride (*e. g.* $3\mathrm{CaP}^2\mathrm{O}^6 = \mathrm{Ca}^3\mathrm{P}^2\mathrm{O}^8 + 2\mathrm{P}^2\mathrm{O}^5$), are partially reduced. The first step therefore in the manufacture of phosphorus consists in the production of calcic metaphosphate.

Bones are burnt to a white ash which is finely powdered and mixed with a quantity of dilute sulphuric acid sufficient to abstract two-thirds of the calcium from the calcic triphosphate and to decompose the whole of the calcic carbonate contained in the bone-ash. About 3 pts. bone-ash and 2 pts. strong sulphuric acid mixed with 18 pts. water are the proportions generally employed:

$$\overset{\prime\prime}{\mathrm{Ca}}{}^3\mathrm{P}^2\mathrm{O}^8 + 2\mathrm{H}^2\mathrm{SO}^4 = \mathrm{Ca}''\mathrm{H}^4\mathrm{P}^2\mathrm{O}^8 + 2\mathrm{Ca}''\mathrm{SO}^4.$$

After subsidence, the soluble monocalcic phosphate (superphosphate of lime) is strained and pressed from the insoluble gypsum, which is slightly washed with water. The washings are added to the phosphate solution, which is then evaporated to a syrup, mixed with about one-fourth its weight of charcoal powder, and heated gradually to dull redness in an iron pot, stirring all the time. By this means the basic water of the monocalcic phosphate is drawn off, and a porous mixture of charcoal and metaphosphate is obtained:

$$\mathrm{Ca}''\mathrm{H}^4\mathrm{P}^2\mathrm{O}^8 = \mathrm{Ca}''\mathrm{P}^2\mathrm{O}^6 + 2\mathrm{H}^2\mathrm{O};$$

and on distilling this mixture at a bright red heat, phosphorus is set free and passes over in vapour, which may be condensed under water; carbonic oxide also escapes and tricalcic phosphate is reproduced and remains behind:

$$3\mathrm{Ca}''\mathrm{P}^2\mathrm{O}^6 + \mathrm{C}^{10} = \overset{\prime\prime}{\mathrm{Ca}}{}^3\mathrm{P}^2\mathrm{O}^8 + 10\mathrm{CO} + \mathrm{P}^4.$$

By mixing sand with the charcoal-paste, as recommended by Wöhler, the whole of the phosphorus may be expelled, the calcic phosphate being entirely converted into silicate:

$$2\mathrm{Ca}''\mathrm{P}^2\mathrm{O}^6 + 2\mathrm{SiO}^2 + \mathrm{C}^{10} = 2\mathrm{Ca}''\mathrm{SiO}^3 + 10\mathrm{CO} + \mathrm{P}^4.$$

The distillation is performed in an earthen retort *a* (*fig.* 735), which is coated externally with a thin paste consisting of a mixture of equal parts of borax and fire-clay to render the retort less porous. The heat is slowly raised to full redness, and the phosphorus, which rises in vapour, is conveyed by a wide copper tube, bent as at *b*, so as to dip into water contained in a vessel provided with a smaller tube for conveying the uncondensed gases into a chimney. The phosphorus condenses in yellow drops which sink to the bottom of the water, without coming in contact with the air. On the large scale a number of retorts containing the mixture are heated in a galley-furnace.

According to calculation the yield of phosphorus by the method above described (not using sand) should amount to 11 per cent. of the bone-ash, and in carefully conducted operations this amount is in fact obtained, but the average yield does not exceed 8 per cent., the loss arising principally from difficulties in the process of distillation. The consumption of fuel is also very large, and the cost of the process is greatly increased by the frequent breakage of the earthen retorts. It has not yet been found possible to obviate these inconveniences in the process, and accordingly the efforts of manufacturers have rather been directed to make up for the unavoidable losses involved in the preparation of phosphorus, by a judicious application of the secondary products, especially by making use of the animal matter of the bones, which was formerly allowed to burn away.

With this view the bones are first freed from fat by boiling them with water and skimming off the liquid fat which floats on the surface; this fat may be used for the preparation of soap. The bones are then either subjected to the action of superheated steam, whereby the gelatinous matter is extracted, and the remaining earthy matter, after being dried and calcined, is used for the preparation of phosphorus as above described; or they are treated with dilute hydrochloric acid, which dissolves out the earthy matter and leaves the cartilaginous substance in a state available for the preparation of gelatin; and the acid solution is precipitated with milk of lime, or better with crude carbonate of ammonia, whereby tricalcic phosphate is obtained, to be used as above.

*Fig.* 735.

Another mode of operation consists in subjecting the bones to destructive distillation, whereby ammonium-salts and bone-charcoal are obtained. The latter is either first used in the refining of sugar, and after it has become unavailable for this purpose calcined for the preparation of phosphorus; or it is purified by exhaustion with hot hydrochloric acid, and the solution separated from the purified charcoal (*noir purifié*) is transformed as above into tricalcic phosphate.

Of late years, processes of manufacture have been proposed which dispense with the necessity of decomposing the bones with sulphuric acid. **Fleck** (Polyteckn. Centralbl. 1856, p. 681; Pharm. J. Trans. xvi. 173) macerates the bones with dilute hydrochloric acid, and evaporates the decanted solution to such a degree of concentration, that on cooling it deposits crystals of acid phosphate of calcium. This salt, after being freed from mother-liquor by pressure between porous stones, is mixed with a fourth part of its weight of wood-charcoal and distilled.

**Cary-Mantrand** (Compt. rend. xxxvi. 854) passes hydrochloric acid gas over a mixture of bone-phosphate and charcoal at a red heat, whereby the whole of the phosphorus is set free and chloride of calcium remains:

$$\ddot{\mathrm{Ca}}{}^3\mathrm{P}^2\mathrm{O}^8 + \mathrm{C}^8 + 6\mathrm{HCl} = 3\mathrm{Ca}''\mathrm{Cl}^2 + 8\mathrm{CO} + \mathrm{H}^6 + \mathrm{P}^2.$$

This mixture is introduced into fire-clay cylinders open at both ends, laid horizontally in a furnace, connected at one end with an apparatus for generating hydrochloric acid gas, and provided at the other with copper adapters dipping into receivers containing water. At the close of an operation, the residue of chloride of calcium and charcoal may be removed from the cylinders and a fresh charge introduced, without putting out the fire. The chloride of calcium may be decomposed by sulphuric acid, so as to yield hydrochloric acid for the next operation. It does not appear however that either this or the preceding process has yet been adopted on the manufacturing scale, the old process by **Nicolas** and **Pelletier** being that which is invariably used.

*Purification*.—The crude phosphorus obtained by the first distillation is contaminated with oxides of phosphorus, red phosphorus, and other substances which give it a red or brown colour. It is purified by mechanical filtration or pressure through chamois-leather, by redistillation, or finally by chemical means, viz. by fusion and partial oxidation. The old method of pressing through chamois-leather appears to be no longer in use, the supply of chamois-leather in fact not being sufficient for the purification of the large quantities of phosphorus now manufactured. The filtration through slabs of chamotte-stone, or layers of charcoal, introduced into French manufactories, has been abandoned as too slow. The purification of phosphorus by redistillation is simpler, but is attended with some loss and involves a considerable expenditure of fuel.

In most manufactures, the purification of phosphorus is now successfully and economically effected by treating the crude product with sulphuric acid and chromate of potassium, as first suggested by **Wöhler**. For this purpose a mixture of chromate of potassium and sulphuric acid is added to the melted mass of crude phosphorus. The red phosphorus appears then to be oxidised first, and the impurities rise to the surface in the form of a scum, while the pure phosphorus remains colourless and transparent at the bottom of the vessel.

*Moulding.*—Phosphorus is frequently sent into the market in sticks. This shape was formerly given to it by drawing the melted phosphorus into glass tubes with the mouth, care being taken to keep the upper part of the tube filled with water. This dangerous method has however been entirely superseded by the following, devised by **Seubert** (Ann. Ch. Pharm. xlix. 346).—The phosphorus is liquefied in an elliptical or conical vessel containing water, which is kept exactly at the melting point of phosphorus (44° C. or 111° F.). From the bottom of this vessel there proceeds an elbow-tube, connected by a socket and stopcock with a horizontal glass tube soldered into the side of a vessel containing cold water. On opening the cock, the liquid phosphorus flows into the horizontal tube, where it solidifies; and by thrusting a copper wire a little way into the tube, allowing the phosphorus to solidify around it, and then gradually withdrawing the wire with the stick of phosphorus adhering to it, the melted phosphorus will continue to flow into the tube and solidify, and may then be drawn out into a long cylinder, which may afterwards be cut into sticks of any required length.

The same apparatus may be used for the granulation of phosphorus. For this purpose, the vessel containing the horizontal tube is filled with cold water only to just below the level of that tube, and upon it is carefully poured a layer of warm water, a thin board being interposed to prevent the warm water from at once mixing with the cold. On opening the stopcock to a moderate extent, the melted phosphorus flows to the end of the horizontal tube and falls out in successive drops, which solidify in passing through the cold water, and collect at the bottom in grains.

Phosphorus may also be granulated by agitating it, while in the fused state, with a warm liquid till it solidifies. For this purpose, according to **Cassarca** (J. Pharm. xvi. 202), alcohol of 36° B. is better adapted than water. According to **Böttger** (*Beiträge zur Chemie und Physik*. i. 65; ii. 127), the liquid which reduces phosphorus to the finest state of granulation is human urine; and it derives this property from the urea which it contains, so that an aqueous solution of artificial urea may be used as a more cleanly substitute for the urine. A tall cylinder an inch wide is half filled with a liquid of this kind, and heat applied till the phosphorus introduced into it is melted: the phosphorus is then worked about for two minutes, by means of a twirling stick which passes through the opening of the wooden cover of the cylinder; it is thus brought into a fine state of division. The remaining portion of the cylinder is then filled with cold water, the twirling motion being continued all the while. When the liquid comes to rest, the phosphorus is deposited in the state of powder; the liquid is then poured off, and the phosphorus washed with water. Respecting the supposed mode of action of the urea, see **Schiff** (Ann. Ch. Pharm. cxviii. 88). **Blondlot** (J. Pharm. [4] i. 72) recommends the use of sugar or of a salt in place of urea.

To the larger manufacturers of lucifer-matches the phosphorus is often supplied in solid cakes or cheeses.

For further details on the preparation and purification of phosphorus, see **Richardson** and **Watts's** *Chemical Technology*, vol. i. pt. 4, pp. 110—125; also **Hofmann's** *Report on Chemical Products and Processes in the Exhibition of* 1862, pp. 93—96.

*Properties.*—Phosphorus, when freshly prepared and quite pure, is almost perfectly transparent and colourless, or with only a faint yellowish tinge. It melts at 44°, forming a viscid oily liquid which sometimes retains its fluidity when cooled several degrees below the melting point, but solidifies instantly when touched with a solid body. The specific gravity of ordinary phosphorus is variously stated at from 1·77 (*Berz. Lehrb.* i. 218) to 2·09 (**Böttger**, in *Gmelin's Handbook*). According to **Gladstone** and **Dale** (Phil. Mag. [4] xviii. 30), the specific gravity of solid phosphorus at 53° is 1·823; that of phosphorus remaining liquid below its melting point, 1·763. It is a non-conductor of electricity both in the solid and in the liquid state.

In warm weather phosphorus is somewhat flexible and may be bent without breaking, but near the freezing point it becomes brittle. When phosphorus is broken, it exhibits a crystalline fracture, but distinctly formed crystals of phosphorus cannot be obtained by fusion, except when a very large quantity is operated on. Crystals of phosphorus may be obtained by cooling a hot saturated solution of phosphorus in rock-oil, or in sulphide of phosphorus, or by the evaporation of its solution in sulphide of carbon. The crystals of phosphorus are usually either regular octahedrons, or rhombic dodecahedrons.

Phosphorus boils in closed vessels at 250° (Heinrich), 288° (Dalton), 290° (Pelletier, Ann. Chem. iv. 3). Its vapour-density, according to Deville and Troost (Bull. Soc. Chim. v. 434), is 4·35 at 500° and 4·50 at 1040° referred to air as unity. The former number gives for the specific gravity of the vapour referred to hydrogen as unity, the number 62·1, which is rather more than double the atomic weight of phosphorus. Hence it appears that the atom of phosphorus in the gaseous state occupies only half the bulk of an atom of hydrogen (see GASES, COMBINATION OF BY VOLUME, ii. 810).

Phosphorus is insoluble in *water*, slightly soluble in *ether*, but more so in *benzene, oil of turpentine* and other *essential* as well as in *fixed oils*. It is also freely dissolved by *chloride of sulphur, trichloride of phosphorus* and *sulphide of carbon*.

Phosphorus is extremely inflammable, taking fire in the open air at a temperature very little above its melting point, burning with a brilliant white flame, and emitting dense white fumes of phosphoric anhydride. If it contains impurities it takes fire still more easily, the heat developed by slight friction being often sufficient to inflame it. Phosphorus must therefore be handled with great caution; a burn from it is very severe and difficult to heal. It must always be kept under water till wanted for use; it may then be taken out and dried by gentle pressure between filtering paper; it is best also to cut it under water. When a solution of phosphorus in sulphide of carbon is dropped upon filtering paper and left to evaporate in the open air, the finely divided phosphorus which remains on the paper absorbs oxygen so rapidly that it immediately takes fire.

The flame of hydrogen-gas impregnated with phosphorus, as produced by the introduction of free phosphorus, hypophosphorous acid or phosphorous acid into Marsh's apparatus (i. 362), exhibits when examined by the spectroscope two intense green lines, one of which coincides with a line in the barium-spectrum. This reaction is so delicate that it will distinctly indicate the presence of phosphorus in the hydrogen evolved on dissolving ordinary iron wire in dilute sulphuric acid (Christofle and Beilstein, Compt. rend. lvi. 399), see also Segnin (*ibid.* liii. 1272).

Phosphorus, when exposed to the air at ordinary temperatures, gradually absorbs oxygen and undergoes a slow combustion, giving off a white vapour which has a peculiar garlic odour, and consists of phosphorous anhydride mixed with a little phosphoric anhydride, or if the air is moist, of the corresponding acids (p. 499). In a dark room the slowly burning phosphorus and the vapour given off from it shine with a greenish-white light.

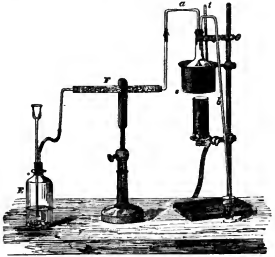
The slow combustion of phosphorus is affected by several circumstances. In pure oxygen of ordinary density it does not take place at all at temperatures below 15°, but on rarefying the oxygen, or diluting it with nitrogen, hydrogen or carbonic anhydride, the phosphorus becomes luminous in the dark at lower temperatures.[*] In the air, the luminosity is not perceptible at temperatures more than a few degrees below 0°, but becomes sensible at that temperature and increases at a few degrees above it. Slow combustion is completely prevented by the admixture of certain inflammable vapours and gases in minute quantity with the air; thus if air be mixed with $\frac{1}{450}$ of its bulk of olefiant gas, $\frac{1}{1820}$ of rock-oil or $\frac{1}{4444}$ of oil of turpentine vapour, a stick of phosphorus no longer becomes luminous when exposed to it.

Respecting the reactions of phosphorus with *chlorine, sulphur* and other elements, see page 505.

*Modifications of Phosphorus.*—Phosphorus is capable of assuming several different forms under the influence of causes apparently trifling.—*α*. When exposed for some time to light under water, it becomes *white*, opaque and scaly, the change proceeding from the surface inwards. This white phosphorus has a specific gravity of 1·515; it is somewhat less fusible than the transparent variety, and is reconverted into the latter by a temperature not exceeding 50°.—*β*. Another modification is produced by the sudden cooling of melted phosphorus; it then becomes perfectly *black* and opaque, but is restored to the transparent colourless condition by simple fusion and slow cooling. According to Blondlot (Compt. rend. lx. 830; Bull. Soc. Chim. [2] iii. 415), this black modification is the type of pure phosphorus. He obtains it by first purifying ordinary phosphorus by several distillations (in hydrogen gas), then exposing it to the sun and distilling again. The product collected in a receiver cooled very slowly solidifies to a white mass which suddenly turns black when the temperature of the condensing water falls to 5° or 6°. It is important, however, to know whether the hydrogen used in the distillation was absolutely pure; since the least trace of certain metals or metalloïds would be sufficient to blacken the phosphorus.—*γ*. A *viscous* modification, analogous to viscous sulphur, may be obtained by heating very pure phosphorus to near its melting point, and suddenly cooling it.

δ. *Red* or *Amorphous Phosphorus.*—This, which is the most remarkable modification of phosphorus, is produced when ordinary phosphorus is exposed to the action of light or heat in an atmosphere not containing oxygen, or when it is heated with a small quantity of iodine. It appears to have been first noticed by Berzelius, who found that phosphorus under the influence of coloured light acquires a red tint, without alteration of weight, and at the same time loses its property of shining in the dark. Subsequently in 1844, Emile Kopp (Compt. rend. xlix. 346) in preparing iodide of ethyl by treating alcohol with iodine and phosphorus, observed the formation of a red modification of phosphorus, amorphous, destitute of taste and odour, very little disposed to oxidise at ordinary temperatures or even at the heat of the water-bath, and reconvertible into ordinary phosphorus by dry distillation. These observations were confirmed by Berzelius (*Rapport Annuel*, 1856, p. 435), and by Marchand (J. pr. Chem. xxxiii. 182). Nevertheless the red modification of phosphorus did not attract much attention till 1858, when Schrötter showed that it might be prepared by simply exposing ordinary phosphorus to light, or more readily by heating it to near its boiling point in an atmosphere free from oxygen, and published a detailed account of its properties (Pogg. Ann. lxxxi. 276). Brodie afterwards showed (in 1852) that amorphous phosphorus may be produced by heating phosphorus with a small quantity of iodine in a sealed tube or in an atmosphere of carbonic anhydride, or by melting phosphorus under strong hydrochloric acid, and then adding a small quantity of iodine. (Chem. Soc. Qu. J. v. 289.)

*Fig.* 736.



Amorphous phosphorus may be prepared on the laboratory scale by placing a quantity of dried common phosphorus in the bulb of a flask A (*fig.* 736) to the neck of which is attached a long narrow tube *b* bent downwards and dipping into mercury; the air in the flask is displaced by means of a current of carbonic anhydride, which is supplied from the bottle E, and dried by passing through the tube F, filled with chloride of calcium; the tube is then sealed at the narrow portion *a*, and the apparatus which supplied the carbonic anhydride is removed. Heat is next applied to the flask by means of an oil-bath *e*. The phosphorus melts readily, but by regulating the heat steadily between 230° and 235° by means of the thermometer *t*, and maintaining it at that temperature for thirty or forty hours, almost all the phosphorus will be brought into the solid amorphous state.

The apparatus just described is similar in principle to that invented and patented by Mr. Albright of Oldbury near Birmingham for the preparation of amorphous phosphorus on the large scale. In this apparatus the phosphorus is heated in a conical glass vessel placed within an iron vessel of the same shape, which is heated by a bath of tin and lead. The melting vessel is provided with a tight-fitting cover, from which there proceeds a safety tube dipping into mercury, as in the apparatus above described. It is not found necessary to expel the air from the apparatus by means of carbonic anhydride, as the small portion of oxygen contained in it is soon consumed by the combustion of a portion of the phosphorus. (For a figure and full description of this apparatus, see Richardson and Watts's *Chemical Technology*, vol. i. pt. 4, p. 127.)

Amorphous phosphorus prepared as above always contains a certain quantity of unaltered phosphorus, which is removed by washing it two or three times with sulphide of carbon, in which common phosphorus is soluble, and red phosphorus insoluble. It has been recommended by Nickles, in order to avoid the use of much sulphide of carbon—a dangerous as well as disagreeable substance—to purify red phosphorus by suspending the finely divided mixture of yellow and red phosphorus in a solution of chloride of calcium of specific gravity about 2·0. In such a solution common phosphorus floats, while red phosphorus sinks.

Red phosphorus is much less fusible than common phosphorus; it may be heated to 250° without alteration, but at 260° it is reconverted into ordinary phosphorus. It also differs from ordinary phosphorus by being insoluble in many liquids in which the latter is soluble, such as sulphide of carbon, alcohol, ether, turpentine, and trichloride of phosphorus. The two modifications differ also not less in chemical than in physical properties. Common phosphorus, as already observed, oxidises slowly in the air at common temperatures, and burns rapidly when heated to about 60°; red phosphorus, on the contrary, is not at all oxidised in the air at common temperatures, emits no odour, and does not become luminous until heated to nearly 260°, the point at which it is transformed into the ordinary modification. Hence it is not liable to take fire by moderate friction, and may be handled without danger, and preserved in bottles, or even wrapped up in paper without liability to alteration. Its properties differ however in some respects according to the mode of preparation. If prepared by heat it has a specific gravity of 2·14: but that which is obtained by the action of iodine on common phosphorus has a specific gravity of 2·23. The latter also volatilises like arsenic, without previous fusion, and condenses to a hard black mass. It is more readily acted on by caustic potash than the former, and precipitates certain metallic solutions, sulphate of copper for example. (Brodie.)

*Reactions of Phosphorus.*—The action of *oxygen* on ordinary and red phosphorus has been already described. With *sulphur* ordinary phosphorus unites rapidly when the two bodies are melted together, the combination being attended with vivid combustion and loud explosion. Red phosphorus, on the other hand, does not unite with sulphur till heated considerably above the melting point of the latter, and even then the combustion, though rapid, is not explosive. *Selenium* unites with phosphorus when the two are heated together nearly to the melting point of the latter.

*Hydrogen* passed over phosphorus contained in a glass tube takes up a small quantity of it, sufficient to colour the flame green, but no definite compound appears to be formed. But when phosphorus, a metallic phosphide, hypophosphorous or phosphorous acid is introduced into an apparatus for generating hydrogen, the evolved gas appears to contain a certain quantity of phosphoretted hydrogen (Dusart, Compt. rend. xliii. 1126).—*Ammonia* acts gradually on ordinary phosphorus, producing phosphoretted hydrogen and a compound of ammonia with an oxide of phosphorus, which, when alcoholic ammonia is used, is deposited on the sides of the tube as a deep black metallic film not decomposed by boiling potash or sulphuric acid. Red phosphorus has no action on ammonia. (Flückiger, Anal. Zeitschr. ii. 398.)

Ordinary phosphorus unites directly at ordinary temperatures. with *chlorine*, bromine and iodine, the combination taking place rapidly and being attended with inflammation. Red phosphorus also unites with these elements at ordinary temperatures, the combination being attended with evolution of heat, but seldom sufficient to produce ignition.

*Chloride of sulphur*, $S^2Cl^2$, dissolves ordinary phosphorus abundantly, and on heating the solution a violent reaction takes place, attended with ebullition and projection of the mass. The same violent action is produced on dipping a stick of phosphorus into a column of chloride of sulphur of about the same depth and volume. On gradually adding small pieces of phosphorus to chloride of sulphur gently warmed in a retort filled with carbonic anhydride, a rapid action also takes place, the liquid becoming hot and distilling over: gradually, however, sulphur separates and the action becomes more moderate; and on mixing the distillate just mentioned with that which afterwards passes over on heating the residue, and redistilling the whole over half its bulk of phosphorus, a colourless liquid is obtained, which separates by fractional distillation into pentachloride and sulphochloride of phosphorus, $PSCl^3$. When chloride of sulphur is gradually poured into melted phosphorus the only products are pentachloride of phosphorus and a yellow sublimate which appears to be a sulphide of phosphorus: the residual phosphorus is converted into the red modification. (Wöhler and Hiller, Ann. Ch. Pharm. xciii. 274.)

Most *metals* unite directly with phosphorus when the latter is thrown upon them while they are in a state of ignition or when they are heated in its vapour.

Finely divided phosphorus, under the influence of sunlight, slowly decomposes

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*water*, forming phosphoretted hydrogen and a red substance commonly regarded as an oxide of phosphorus.

Many *acids* are decomposed when heated with phosphorus, yielding phosphorous acid, together with other products.—Pure concentrated *hydriodic acid* heated with amorphous phosphorus to 160° for two hours yields phosphorous acid, and sublimed crystals of hydriodate of phosphoretted hydrogen.—*Hydrobromic acid* acts in a similar manner, but somewhat more slowly.—Pure concentrated *hydrochloric acid* heated with amorphous phosphorus to 200° for sixteen hours appears to be decomposed according to the equations: $3HCl + P^2 = PH^3 + PCl^3$; and $PCl^3 + 3H^2O = PH^3O^3 + 3HCl$. Strong *sulphuric acid* is reduced to sulphurous anhydride, which floats on the surface of the phosphorous acid formed at the same time:

$$3SH^2O^4 + P^2 = PH^3O^3 + 3SO^2.$$

*Sulphurous acid* yields phosphorous and sulphydric acids:

$$SH^2O^3 + 3H^2O + P^2 = 2PH^3O^3 + H^2S.$$

Syrupy *phosphoric acid* heated to 200° with phosphorus for forty hours, is reduced to hypophosphorous acid, which latter is partly resolved into phosphorous acid and phosphoretted hydrogen.—Aqueous *chromic acid* heated with phosphorus is reduced to chromoso-chromic oxide; *arsenious acid* yields phosphide of arsenic. (Oppenheim, Bull. Soc. Chim. [2] i. 163.)

Phosphorus boiled with aqueous *alkalis* and *alkaline earths* forms phosphoretted hydrogen and a solution of a hypophosphite, *e. g.* with lime-water:

$$3Ca''H^2O^2 + P^8 + 6H^2O = 3Ca''H^4P^2O^4 + 2PH^3.$$

Phosphorus likewise decomposes many other oxides and salts, both in the dry and in the wet way. When rubbed with *chlorate of potassium*, it detonates and takes fire, a slight friction being sufficient to induce the reaction. *Nitrate of potassium* and the *peroxides of lead* and *manganese* act upon it in a similar manner, but less violently. When a mixture of *carbonate of sodium* and amorphous phosphorus is heated in a combustion tube to low redness, or better to 240° only, a brown mass is obtained, which takes fire on exposure to the air, and when thrown into water gives off a large quantity of spontaneously inflammable phosphoretted hydrogen, and forms a dark brown solution, from which hydrochloric acid throws down brown flocks, forming when dry a black-brown amorphous mass containing about 40 per cent. of humus-like bodies. When carbonate of sodium is heated to redness with excess of phosphorus, the whole of the carbon is set free; with excess of sodic carbonate, on the other hand, a mixture of charcoal, sodic phosphate and sodic carbonate is obtained, carbonic oxide being given off and phosphorus distilling over. The carbon obtained in these reactions has a deep velvet-black colour, a specific gravity of 1·46 at 14°, and possesses strong absorbent and decolorising properties. Phosphorus acts in like manner on other carbonates, also on borates and silicates. (Dragendorff, Jahresb. 1861, p. 110.)

Phosphorus placed in contact with many metals in solutions of the same metals, produces an electric current, and precipitates the metals. In contact with clean copper wire in a solution of cupric sulphate, it precipitates the copper on the wire in octahedral crystals (Wöhler, Ann. Ch. Pharm. lxxix. 126). In like manner it reduces *silver* and *lead* from the solutions of their nitrates (Wicke, *ibid.* lxxii. 145). Phosphorus immersed in a solution of *potassic permanganate* forms peroxide of manganese and phosphate of potassium. Neutral and acid *chromate of potassium* are incompletely decomposed by phosphorus at common temperatures with formation of potassic and chromic phosphates. *Cupric chromate* boiled with phosphorus yields metallic copper, phosphide of copper, and chromic phosphate. A solution of potassic chlorate boiled with phosphorus is converted into phosphite, phosphate, and chloride of potassium. *Nitrate of barium* is not decomposed by boiling with phosphorus; *nitrate of lead* yields a deposit of phosphate of lead; *nitrate of copper* in concentrated solution yields cupric oxide and phosphide of copper; in dilute solution, metallic copper, phosphide of copper, and phosphoric acid. (Slater, Chem. Gaz. 1853, p. 329.)

*Chemical Relations of Phosphorus.*—Phosphorus belongs to the pentad group of elements (iii. 967), including also nitrogen, arsenic, antimony and bismuth. Its pentatomic character is exhibited in the pentachloride $P^vCl^5$, the oxychloride $P^v\left\{\begin{matrix}Cl^3\\O''\end{matrix}\right.$, phosphoric triethodichloride (or chloride of triethyl-phosphine) $P^v\left\{\begin{matrix}(C^2H^5)^3\\Cl^2\end{matrix}\right.$, &c., also in phosphoric anhydride $\left.\begin{matrix}P^v\\P^v\end{matrix}\right\}O^5$, and in phosphoric acid regarded as $\left.\begin{matrix}P^v\\H^3\end{matrix}\right\}O^4$. But it likewise, and perhaps more frequently plays, the part of a triatomic element, as in phosphoretted hydrogen or phosphine $P'''H^3$, and its alcoholic derivatives triethyl-phosphine $P'''(C^2H^5)^3$, &c., also in trichloride of phosphorus $P'''Cl^3$, phosphorous anhydride

$\left.\begin{matrix}P''' \\ P'''\end{matrix}\right\}O^3$, &c., phosphorous acid $\left.\begin{matrix}P''' \\ H^3\end{matrix}\right\}O^3$, &c., In some few compounds also it is diatomic, as in the di-iodide $PI^2$, and perhaps in liquid phosphide of hydrogen $PH^2$ (iii. 204); in many of its metallic compounds it exhibits still lower degrees of atomicity.

In its triatomic and pentatomic character, phosphorus resembles the other members of the group above mentioned. It is most closely related to arsenic and antimony, each of these elements forming a gaseous trihydride, and their chlorides, bromides and oxides being exactly analogous to one another in composition. To arsenic it is further related by the strictly analogous composition and the isomorphism of the corresponding phosphates and arsenates, and by its anomalous vapour-volume, the specific gravities of each of these elements in the gaseous state being double its atomic weight (p. 503; also iii. 968). Bismuth is also related to phosphorus, arsenic, and antimony by the composition of its chlorides and oxides, although its pentatomic compounds are not of very stable character. To nitrogen, phosphorus is related by its combination with hydrogen, and by its formation of anhydrides with 3 and 5 atoms of oxygen.

The elements of this group exhibit in many respects a regular gradation of properties in the order of their atomic weights. Nitrogen (14) is gaseous, while all the rest are solid at ordinary temperatures, and of these latter phosphorus (31) is the most fusible and volatile; next follows arsenic (75), then antimony (122), and lastly bismuth (210). The acid properties of the oxidised compounds are most marked in nitrogen, then in phosphorus; they are weaker in arsenic, still weaker in antimony, and scarcely apparent in bismuth. The compounds with hydrogen follow in the same order; ammonia is a powerful base, and requires a high temperature for its decomposition; phosphine, $PH^3$, is a very feeble base; in arsine, $AsH^3$, the basic character is not perceptible, though manifested in triethyl-arsine and other of its derivatives; the same is true of the corresponding antimony-compounds. Each of the three hydrides last mentioned is decomposed by simple exposure to heat, phosphine requiring the highest temperature, arsine decomposing at a lower, and stibine at a still lower degree of heat, while the affinity of bismuth for hydrogen is so feeble that it does not appear to form a hydride.

USES OF PHOSPHORUS.—The chief use of phosphorus is for the preparation of the paste with which lucifer matches are tipped; for this purpose both the ordinary and the amorphous variety of phosphorus are employed. Ordinary phosphorus, being intensely poisonous, is also used in the formation of compositions for poisoning rats, cockroaches and other vermin; and both kinds are used in a variety of ways in chemical and pharmaceutical preparations.

A phosphorated paste for poisoning vermin may be prepared by dissolving 250 pts. by weight of gum arabic in 500 pts. of water at 140° F., adding 15 pts. of phosphorus, stirring as it melts, then removing the vessel from the fire and continuing the stirring as the mixture cools in order to thoroughly incorporate the phosphorus. The mixture is then placed over the water-bath, the stirring being still continued; a paste previously made up with 100 pts. of flour, or better of potato-starch, and 100 pts. of water is added to it, and the whole is beaten up for half an hour at 122° F., after which it is left to cool, the agitation being still continued till the temperature has fallen to 86°. The process yields from 500 to 5[illegible]0 pts. of phosphorated paste. To effect a still finer division of the phosphorus, the paste may be ground under the muller.

*Lucifer-matches.*—Ordinary lucifer-matches are simply wooden sulphur-matches tipped with a paste containing phosphorus, and capable of igniting by friction. The materials added to the phosphorus to promote its ignition are chlorate or nitrate of potassium, or certain metallic oxides which easily give up their oxygen, such as the peroxides of lead and manganese. Chlorate of potassium causes the paste to ignite with detonation when rubbed, and often occasions the projection of a portion of the burning matter to a considerable distance. This projection, which is rather dangerous, may be prevented by using nitrate instead of chlorate of potassium; the matches then burn quietly.

The phosphorus, and the salt or oxide which is to supply it with oxygen for combustion, are made up into a paste with a strong solution of glue or gum, a small quantity of vermillion or Prussian blue being added as colouring matter, and sometimes a little fine sand to increase the friction.

The proportion of phosphorus varies considerably, being sometimes as high as 30 or even 50 per cent. and sometimes as low as 10 or even 5 per cent. The following are two compositions recommended by Böttger in 1844, and still in use for the preparation of noiseless lucifers:

| | | | |
|---|---|---|---|
| Phosphorus (ordinary) | 4 | Phosphorus (ordinary) | 9 |
| Saltpetre | 16 | Saltpetre | 14 |
| Red lead | 3 | Peroxide of manganese | 14 |
| Strong glue | 6 | Gum | 16 |

The reduction of the proportion of phosphorus in the inflammable mass to a minimum is a great desideratum, as the process is thereby rendered less costly, and the matches when ignited emit less of the disagreeable odour of phosphorus. A good method of effecting this reduction is that recommended by R. Wagner (Wagner's Jahresbericht, 1855, p. 503), which consists in preparing the inflammable mass with phosphorus dissolved in sulphide of carbon. This process not only effects the perfect molecular subdivision of the phosphorus, but it enables the mass to be prepared without the use of heat, a further very great advantage. According to E. Mack (Verhandl. des Vereins f. Naturkunde in Presburg, 1858, i. 17), this simple expedient renders it possible to reduce the proportion of phosphorus to $\frac{1}{326}$ of that at present in common use.

Some matches, instead of being coated at the ends with sulphur, are impregnated throughout with stearic acid, wax, or paraffin. The paste for dipping these matches requires less gum and a more active oxidising agent than that for the sulphur-matches. The following are two of the compositions in use:

| | | | |
|---|---|---|---|
| Phosphorus (ordinary) | 3·0 | Phosphorus (ordinary) | 3·0 |
| Strong glue | 3·5 | Gum tragacanth | 0·5 |
| Water | 3·0 | Water | 3·0 |
| Fine sand | 2·0 | Fine sand | 2·0 |
| Vermillion or Prussian blue | 0·1 to 0·5 | Dioxide of Lead | 2·0 |
| Chlorate of Potassium | 3·0 | | |

The dioxide of lead in the second of these compositions may be replaced by 2 pts. of red lead and 0·5 pts. strong nitric acid.

Matches thus prepared burn more readily than sulphur-matches, because the fatty matter and the wood take fire together, whereas in sulphur-matches the wood does not ignite till the sulphur is nearly consumed. The matches impregnated with fatty matter also burn with a brighter flame, and are free from the suffocating odour which the sulphur-matches evolve in burning. Formerly these matches were impregnated with wax or stearic acid or resin, and as these materials are more expensive than sulphur, their use was confined to the higher priced matches; recently, however, the use of paraffin and paraffin-oils for the purpose, patented by Mr. Letchford of Whitechapel, has greatly reduced the price of matches thus prepared.

*Taper* or *Vesta-matches*, which consist of tapers of wax, rosin and tallow, or paraffin, require to be tipped with a very inflammable paste, because, having but little rigidity, they cannot bear much friction without bending. The paste used for tipping them is made of 12 pts. ordinary phosphorus, 14 gum, 3 sulphide of antimony, 36 dioxide of lead (or 56 pts. of a mixture of red lead 35 pts. and nitric acid 21 pts.) and 0·1 vermillion.

*Fusees* for lighting cigars are made from strips of pulp or thin card-board previously prepared by steeping in a solution of saltpetre.

*Matches with Amorphous Phosphorus.*—The use of ordinary phosphorus in the manufacture of lucifer-matches is attended with certain inconveniences, arising partly from the great facility with which it is set on fire by friction or by a very moderate heat, partly from the slow combustion which it undergoes at ordinary temperatures, whereby acid vapours are produced of very deleterious character. From this cause, the workpeople engaged in the manufacture, especially the dippers, occasionally suffer from a peculiar disease of the jaw, which commences with pain and swelling, and ultimately produces necrosis of the bone. Ordinary phosphorus is, moreover, very poisonous in the solid state, and instances have occurred of children being poisoned by sucking matches tipped with it.

Amorphous phosphorus, on the other hand, is free from all these objections. It is not poisonous in the solid state, and not being volatile or subject to slow combustion at ordinary temperatures, or even at the heat required to keep the paste in the liquid state, it does not impregnate the air of a factory with poisonous vapours. Moreover, it is not liable to be set on fire by accidental friction.

But, notwithstanding these advantages, the use of matches tipped with amorphous phosphorus has not become general. Lucifers of this kind were sent to the Exhibition of 1851 by Messrs. Dixon and Co. of Manchester, but they never found favour with the public, and have of late years disappeared from the market. The chief objections to them seem to be that they are not sufficiently inflammable, and that they burn with a sputtering flame.

Böttger in 1848 suggested the preparation of friction matches capable of taking fire only when rubbed on a surface prepared in a particular way. Such matches, containing no phosphorus in themselves, but supplied in boxes provided with rubbers containing amorphous phosphorus, were first sent into the market by Preshel of Vienna in 1854, and their preparation has since that time been greatly improved by Lundström of Sweden, and by Messrs. Coignet and Co. of Lyons. In this country, patents for the manufacture of lucifers by Lundström's process have been taken out by Messrs. Brysut and May.*

The igniting composition applied to the tips of these matches, and the paste for the rubber are composed as follows:

| *Paste for Matches.* | |
|---|---|
| Chlorate of potassium | 6 pts. |
| Sulphide of antimony | 2 to 3 „ |
| Glue (weighed dry) | 1 pt. |

| *Paste for Rubber.* | |
|---|---|
| Amorphous phosphorus | 10 pts. |
| Oxide of manganese or sulphide of antimony | 8 „ |
| Glue (weighed dry) | 3 to 6 „ |

Matches thus prepared possess the great advantage of being free from all danger of ignition by accidental friction: hence they are called *Safety-matches* (*Allumettes de sûreté*); they are much used in France and other parts of the Continent, and their use appears also to be extending in this country; but the great majority of consumers still exhibit a preference for a match which will ignite by friction on any rough surface.

There is another modification of the same principle, introduced by MM. Desirliers and Dalemagne, in which the amorphous phosphorus is placed at one end of the match, and the chlorate of potassium at the other, so that ignition takes place on breaking the match in halves and rubbing the two ends together. But these matches, called *Allumettes androgynes*, do not appear to have come into actual use.

*Lucifers without Phosphorus.*—To avoid all danger of poisoning in the preparation as well as in the use of lucifer-matches, it has of late years been proposed to tip them with a composition containing no phosphorus whatever, either ordinary or amorphous. Various compositions have been proposed for this purpose; it may be sufficient to mention for illustration one of those patented by G. Canouil (1857, No. 2817), which is composed of chlorate of potassium 75 pts., dioxide of lead 35 pts, iron pyrites 35 pts., and gum, dextrin, or glue 10 pts. Sulphide of antimony and free sulphur, either singly or together, are also used as the inflammable material in these pastes. The most systematic researches on this branch of manufacture have been made by Wiederhold (Dingl. pol. J. clxi. 221, 268; clxiii. 203, 269), from which it appears that matches of good quality may be made with chlorate of potassium and hyposulphite of lead.

The total elimination of phosphorus from the lucifer manufacture would indeed, as observed by Hofmann (*Report*, 1862, p. 99), be a grand achievement, not merely no sanitary grounds, or as diminishing fire-risks, but also because it would immediately liberate for agricultural purposes a large quantity of bones now consumed in the preparation of free phosphorus.

For further details on the chemistry of the lucifer-match manufacture, and for figures and descriptions of machinery used for cutting and dipping the matches, see Richardson and Watts's *Chemical Technology*, vol. i. pt. 4, pp. 131–180.

**PHOSPHORUS, BROMIDES OF.** Phosphorus unites directly with bromine at ordinary temperatures, with evolution of heat, and in the case of ordinary phosphorus, of light: small pieces of ordinary phosphorus thrown into bromine may produce a dangerous explosion. There are two bromides of phosphorus, the tribromide and pentabromide, the former liquid at ordinary temperatures, the latter solid; the one or the other being produced according to the proportions in which the two elements are brought together.

**Tribromide of Phosphorus** or **Phosphorous Bromide.** $PBr^3$.—Produced: 1. By bringing bromine in contact with excess of phosphorus. Phosphorus is added in pieces, not weighing more than a quarter of a grain, to perfectly anhydrous bromine, till the liquid becomes colourless, after which the compound is separated by distillation from the excess of phosphorus (Löwig, Pogg. Ann. xiv. 485). In order to avoid the chance of explosion, it is best to pour the bromine into a wide-mouthed bottle, and introduce perfectly dry phosphorus in a glass tube, sealed at bottom, and placed upright in the liquid, so that on closing the bottle the bromine-vapour may slowly come in contact with the phosphorus (H. Rose, Pogg. Ann. xxviii. 550). An easy mode of preparation is to dissolve bromine and phosphorus in separate portions of sulphide of carbon, then pour the bromine-solution slowly into the phosphorus-solution, and distil (Keknlé, Ann. Ch. Pharm. cxxx. 16).—2. Vapour of phosphorus is passed over mercurous or mercuric bromide, which is heated in a glass tube by means of a spirit-lamp, and the product is collected in a cooled receiver; the product is purified from excess of phosphorus by distillation. (Löwig.)

Tribromide of phosphorus is a colourless, transparent, mobile liquid, which does not freeze even at −12°, is very volatile, and emits dense white fumes in the air; has the pungent odour of hydrobromic acid; it probably reddens litmus paper only when moisture is present. (Löwig; Balard.)

It is decomposed—1. By *water*, with great disengagement of heat, into phosphorous and hydrobromic acids, which latter, when a small quantity only of water is employed, is evolved in the gaseous form (Balard). At 8° the decomposition takes place but slowly, even when the mixture is repeatedly shaken; at 25° it proceeds very rapidly (Löwig). By *chlorine*, into chloride of phosphorus and free bromine. (Balard.)

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* May (F.), Patent No. 1851, Aug. 15, 1855.

Tribromide of phosphorus is capable of dissolving an additional quantity of phosphorus, whereby it acquires the property of setting fire to combustible bodies brought in contact with it in the open air (Balard), of forming a pellicle of phosphorus when exposed to air, and depositing phosphorus when decomposed with water. (Löwig.)

*Ammonio-phosphorous bromide*, $PBr^3.5NH^3$, is formed when ammonia-gas is slowly passed into well-cooled tribromide of phosphorus. It is a white powder which, when heated out of contact with air, is resolved into phosphide of nitrogen, phosphorus-vapour, bromide of ammonium, ammonia and hydrogen gas (Rose). With water it yields bromide and phosphite of ammonium.

**Pentabromide of Phosphorus** or **Phosphoric Bromide.** $PBr^5$. *Perbromide of Phosphorus.*—Produced by the action of bromine in excess on phosphorus or on the tribromide; also by decomposing iodide of phosphorus with bromine; most easily prepared by the second process.

It is a lemon-yellow solid, crystallising in rhomboidal forms after fusion, in needles when sublimed; melts at a moderate heat to a red liquid, which at a higher temperature evolves red vapours; evolves dense pungent fumes in the air. (Balard.)

*Decompositions.*—1. By *chlorine* into chloride of phosphorus and free bromine.—2. By heated *metals*, into metallic bromide and phosphide (Balard).—3. By *oxide of copper* and *red oxide of mercury*, into metallic bromide and phosphate (Löwig).—4. By a small quantity of *water*, into oxybromide of phosphorus, and hydrobromic acid (Gladstone); by a larger quantity, with rise of temperature, into phosphoric and hydrobromic acids (Balard):

$$PBr^5 + H^2O = POBr^3 + 2HBr$$
$$PBr^5 + 4H^2O = PH^3O^4 + 5HBr.$$

5. By dry *sulphydric acid gas*, forming a heavy liquid composed of $P^2S^5.6PBr^3$, which boils at 200° without decomposition, but respecting which it has not been positively determined whether it is a definite compound or a mixture of two substances of equal or nearly equal boiling points (Gladstone, Phil. Mag. [3] xxxv. 345).—6. In *phosphoretted hydrogen gas* the pentabromide first becomes liquid, yielding tribromide of phosphorus and hydrobromic acid, which then unites with another portion of phosphoretted hydrogen, and forms hydrobromate of phosphine $PH^3.HBr$, or bromide of phosphorium $PH^4Br$, which crystallises in cubes (Serullas, iii. 201). By prolonged action of the phosphoretted hydrogen, the whole of the bromine is removed from the pentabromide, and phosphorus is set free.

**PHOSPHORUS, CHLORIDES OF.** Phosphorus unites readily and directly with chlorine even at 0°, the product being a trichloride or pentachloride, according to the proportions of the two elements present. The action of chlorine on ordinary phosphorus is attended with visible combustion. Chlorides of phosphorus are also produced by the action of phosphorus on metallic chlorides.

**Trichloride of Phosphorus** or **Phosphorous Chloride,** $PCl^3$; formerly called *Protochloride of Phosphorus.*—This compound is prepared: 1. By passing dry chlorine gas over phosphorus contained in a tabulated retort till all the air is expelled, then gently heating the phosphorus in a sand-bath, while a slow stream of chlorine is kept up, so that the gas may always come in contact with an excess of phosphorus. The trichloride then condenses in the receiver as an oily liquid, which may be purified from excess of phosphorus by slow rectification. If it contains any pentachloride, which will be the case if the stream of chlorine has been too rapid, it must be digested for some days with phosphorus and then rectified.—2. Dry phosphorus is placed at the closed end of a glass tube; a few lumps of mercuric chloride are placed upon it; the phosphorus is gently heated so that its vapour may pass slowly over the mercuric chloride, and the trichloride of phosphorus thereby produced is collected in a cooled receiver and afterwards rectified.

Trichloride of phosphorus is a thin, transparent, colourless liquid, of specific gravity 1·61 (Pierre), 1·45 (Davy), boiling at 78° to 78·5° under a pressure of 751 to 767 mm. (Dumas, Pierre, Andrews), at 73·8 under a pressure of 760 mm. (Regnault, Jahresb. 1863, p. 70). Vapour-density = 4·79: calc. (2 vols.) = 4·77. Latent heat of vapour = 67·24 (Regnault, Jahresb. 1863, p. 77). The tension of its vapour at different temperatures is according to Regnault (Jahresb. 1863, p. 65) as follows:

| Temperature. | Tension of Vapour. | Temperature. | Tension of Vapour. |
|---|---|---|---|
| 0°C | 37·98 mm. | + 40°C | 341·39 mm. |
| + 10 | 62·88 | 50 | 485·63 |
| 20 | 100·55 | 60 | 674·23 |
| 30 | 155·65 | | |

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Trichloride of phosphorus scarcely reddens litmus-paper. It dissolves *phosphorus* but quickly deposits it again in the amorphous state, on exposure to the air. It absorbs *chlorine* rapidly, forming the pentachloride, and *oxygen*, at the boiling heat, to form the oxychloride (Brodie). When heated in the flame of a spirit-lamp, it takes fire and burns with a bright phosphorous flame. *Potassium* burns brightly in its vapour; red-hot *iron-filings* decompose it with formation of phosphide of iron and ferric chloride. Strong *nitric* or *nitrous* acid decomposes it with violent explosion. (Persoz and Bloch, Compt. rend. xxviii. 86.)

When poured into *water*, it sinks to the bottom and decomposes, yielding hydrochloric and phosphorous acids:

$$PCl^3 \quad + \quad 3H^2O \quad = \quad 3HCl \quad + \quad PH^3O^3.$$

When exposed to moist air it slowly decomposes in the same manner, giving off white pungent acid vapours, and acquiring an acid reaction.

With *sulphydric acid* it forms hydrochloric acid and trisulphide of phosphorus. (Serullas):

$$2PCl^3 \quad + \quad 3H^2S \quad = \quad 6HCl \quad + \quad P^2S^3.$$

With *phosphoretted hydrogen* it forms hydrochloric acid and yellow phosphorus, which quickly turns red on exposure to light.

With *monatomic alcohols*, *ethers*, and *acids*, it acts in the same manner as on water, producing a chloride of the alcohol-radicle, or acid-radicle and phosphorous acid or anhydride, the phosphorous acid sometimes acting further on the alcohol to form a phosphorous ether (Béchamp, Compt. rend. xl. 944; xli. 23). Thus with *ethylic alcohol* it yields chloride of ethyl and phosphorous acid or phosphorous ether:

$$3(C^2H^5.H.O) \quad + \quad PCl^3 \quad = \quad 3C^2H^5Cl \quad + \quad PH^3O^3$$

and $$3(C^2H^5.H.O) \quad + \quad PH^3O^3 \quad = \quad P(C^2H^5)^3O^3 \quad + \quad 3H^2O.$$

Anhydrous *ether* (ethylic oxide or anhydride) does not act on the trichloride at ordinary temperatures, but when the two liquids are heated together to 180°—200° in sealed tubes, chloride of ethyl and phosphorous anhydride are produced, the latter being partly resolved by the heat into phosphoric anhydride and red phosphorus:

$$3(C^2H^5)^2O \quad + \quad 2PCl^3 \quad = \quad 6C^2H^5Cl \quad + \quad P^2O^3.$$

With *acetic acid* and *anhydride* it yields, under similar circumstances, chloride of acetyl and phosphorous acid or anhydride.

Heated with *ethylic acetate* to 160°—180° in a sealed tube, it yields chloride of acetyl, chloride of ethyl, and phosphoric anhydride:

$$3(C^2H^3O.C^2H^5.O) \quad + \quad 2PCl^3 \quad = \quad 3C^2H^3OCl \quad + \quad 3C^2H^5Cl \quad + \quad P^2O^3.$$

From the ethers of the *glycollic* or *lactic series*, $C^nH^{2n}O^3$, it abstracts the elements of water, converting them into ethers of the acrylic series, $C^nH^{2n-2}O^2$, according to the general equation:

$$3C^nH^{2n}O^3 \quad + \quad PCl^3 \quad = \quad 3C^nH^{2n-2}O^2 \quad + \quad PH^3O^3 \quad + \quad 3HCl.$$

(Frankland and Duppa, p. 273.)

*Zinc-ethyl* acts very violently on trichloride of phosphorus, producing triethylphosphine and zinc-chloride:

$$2PCl^3 \; + \; 3Zn''(C^2H^5)^2 \; = \; 3Zn''Cl^2 \; + \; 2P(C^2H^5)^3.$$

Similar products are obtained with *zinc-methyl* and *zinc-amyl* (Hofmann and Cahours). See PHOSPHORUS-BASES.

*Ammonia-gas* is rapidly absorbed by the trichloride, forming, if rise of temperature be prevented by external cooling, a white mass which was formerly regarded as a definite ammonio-trichloride of phosphorus, $5NH^3.PCl^3$, and was supposed to be resolved by heat into ammonia, hydrogen, phosphorus-vapour and a residue of dinitride of phosphorus $PN^2$ (see *Gmelin's Handbook*, ii. 481). But this ammonio-trichloride has never been obtained pure, and its very existence is doubtful. The product of the reaction of ammonia on the trichloride appears indeed to consist mainly of a mixture of sal-ammoniac and phosphoroso-triamide, formed according to the equation, $PCl^3 + 6NH^3 = 3NH^4Cl + N^3H^6P$, and yielding, when ignited without access of air, a residue of phosphoroso-diamide and phosphoroso-monamide (p. 499).

**Pentachloride of Phosphorus** or **Phosphoric Chloride.** $PCl^5$. *Perchloride of Phosphorus.*—This compound is produced by the action of chlorine in excess on phosphorus or on the trichloride.—1. Dry chlorine is passed in a rapid stream into a large retort or Woulfe's bottle containing phosphorus, which must be kept cool at first, as otherwise the heat developed by the reaction will cause the trichloride of phosphorus produced in the first instance to distil over. Afterwards, when the absorption of the chlorine becomes slower, the reaction may be assisted by a gentle heat. Amorphous phosphorus exposed in the state of powder to the action of a rapid stream of chlorine is at once converted into the solid pentachloride.

2. Phosphorus is also rapidly converted into pentachloride when introduced into sulphide of carbon previously saturated with chlorine; and when chlorine is passed to saturation into a solution of phosphorus in sulphide of carbon, the liquid on cooling deposits the pentachloride in crystals. This last method is now much used for the preparation of the compound on the large scale; but according to Hugo Müller (Zeitschr. Ch. Pharm. 1862, p. 295), the pentachloride thus prepared almost always contains free phosphorus, especially when too strong a solution has been used, or the liquid has been too strongly cooled before the formation of the pentachloride is complete. The impure product thus obtained has a dull waxy aspect different from the shining straw-yellow crystalline character of the pure pentachloride, and changes more or less, in course of time, into the liquid trichloride. Moreover, if the proportion of free phosphorus in it is large, it may become dangerous, as the reaction between the free phosphorus and the pentachloride may then be attended with a rise of temperature high enough to produce explosion. The product is also liable to be contaminated with a sulphur-compound, resulting from the action of the sulphide of carbon on the pentachloride. For these reasons Müller recommends the preparation of pentachloride of phosphorus from the trichloride as follows.

3. A small quantity of the trichloride is introduced into a wide-mouthed capacious glass vessel, closed by a perforated caoutchouc plate through which the chlorine is introduced. A certain quantity of phosphorus is then dissolved in it; chlorine gas is passed into the vessel till the whole of the phosphorus is converted into trichloride; a fresh portion of phosphorus is added; more chlorine passed into the vessel; and so on till the necessary quantity of trichloride is obtained. This product is then converted into pentachloride by prolonged exposure to excess of chlorine. In this process the trichloride acts as a solvent of the phosphorus in place of the sulphide of carbon used in the ordinary manufacturing process. If the product obtained by either of the above processes still retains traces of trichloride, it may be purified by redistillation in a stream of chlorine.

*Properties.*—Pentachloride of phosphorus is a white, or more frequently a straw-yellow mass of more or less compact texture; it crystallises from fusion in prisms (Davy). Brodie by passing chlorine into a solution of phosphorus in sulphide of carbon obtained it in distinct rhombic crystals. It sublimes at 100° without previous fusion, but under increased pressure it melts at 148° and boils at a temperature a little above. The specific gravity of its vapour is, according to Mitscherlich, 4·85 at 185°; according to Cahours it varies from 5·078 at 182° to 3·656 at 336°. The last agrees nearly with a condensation to 4 volumes, for $\frac{31 + 5 \,.\, 36{\cdot}5}{4} \times 0{\cdot}0693 = 3{\cdot}693$. Probably a case of dissociation, 2 vols. of the pentachloride splitting up when strongly heated into 2 vols. $PCl^3$, and 2 vols. Cl. (See ii. 817.)

*Decompositions.*—1. Pentachloride of phosphorus burns in the flame of a candle, and when its vapour mixed with *oxygen*, is passed through a red-hot tube, it burns, with formation of phosphoric anhydride and liberation of chlorine, and according to Baudrimont (Rép. Chim. pure, 111, 114), with formation of oxychloride of phosphorus.

2. Treated in like manner with *hydrogen*, it yields hydrochloric acid, trichloride of phosphorus, free phosphorus, and phosphoretted hydrogen. (Baudrimont, *loc. cit.*)

3. It does not act on carbon or on bromine, but with *iodine* it forms pentachloride of iodine, which unites with the excess of the pentachloride, forming the compound $PCl^5.ICl$. The same compound is formed by the action of the pentachloride on *trichloride of iodine*: $PCl^5 + ICl^3 = PCl^5.ICl + Cl^2$; also by the direct union of the pentachloride of phosphorus with protochloride of iodine, or of trichloride of phosphorus with trichloride of iodine. (Baudrimont, Rép. Chim. pure, iv, 60.)

4. Fused with *sulphur*, it yields sulphoperchloride of phosphorus $PCl^5S^2$ or $PCl^3.2SCl$ (Gladstone, Chem. Soc. Qu. J. iii. 5). With *selenium*, it forms the compound $P^2Cl^{14}Se$ or $2PCl^5.SeCl^4$. (Bandrimont.)

5. Heated with various *metals* to 130°—140°, it forms trichloride of phosphorus and a metallic chloride, which generally unites with the excess of pentachloride, forming a double chloride; such is the case with *aluminium*, *bismuth*, *iron*, *tin*, and perhaps also with *zinc* and *copper*. *Gold* and more particularly *platinum* are easily attacked by the pentachloride, the latter yielding the sublimable compound $2PCl^3.PtCl^4$. *Antimony* is the most easily attacked of all metals by phosphoric chloride. If the metals are heated to redness, a much more violent action takes place, phosphorus being set free, and a metallic phosphide sometimes formed (Baudrimont). *Potassium* heated in its vapour burns with a brilliant light.

6. Pentachloride of phosphorus heated with a small quantity of *water*, or exposed to moist air, in which case it gives off a large quantity of intensely pungent acid fumes, is resolved into hydrochloric acid and oxychloride of phosphorus; with a larger quantity of water it yields hydrochloric and phosphoric acids:

$$PCl^5 + H^2O = POCl^3 + 2HCl.$$

$$\text{and } PCl^5 + 4H^2O = PH^3O^4 + 5HCl.$$

7. *Sulphydric acid* in like manner converts it into hydrochloric acid and sulphochloride of phosphorus:

$$PCl^5 + H\,S = PSCl^3 + 2HCl.$$

8. By *alcohols* and *acids* it is decomposed in the same manner as by water, yielding hydrochloric acid, a chloride of the alcoholic or acid radicle, and oxychloride of phosphorus, or phosphoric acid, according to the proportions of the acting substances, the phosphoric acid thus formed acting further on the alcohol to produce a phosphoric ether; thus with amylic alcohol:

$$\underset{\text{Amylic alcohol.}}{C^5H^{11}.H.O} + PCl^5 = \underset{\text{Chloride of amyl.}}{C^5H^{11}Cl} + HCl + POCl^3.$$

$$\text{and } 9(\underset{\text{Amylic alcohol.}}{C^5H^{11}.H.O}) + 2PCl^5 = \underset{\text{Chloride of amyl.}}{5C^5H^{11}Cl} + 5HCl + 2[\underset{\text{Diamylic phosphate.}}{(C^5H^{11})^2HPO^4}] + H^2O$$

$$\underset{\text{Acetic acid.}}{C^2H^4O^2} + PCl^5 = \underset{\text{Chloride of acetyl.}}{C^2H^3OCl} + HCl + POCl^3.$$

$$\underset{\text{Lactic acid.}}{C^3H^6O^3} + 2PCl^5 = \underset{\text{Chloride of lactyl.}}{C^3H^4OCl^2} + 2HCl + 2POCl^3.$$

With some diatomic acids, however, it first forms the corresponding anhydrides, which are then converted by excess of the pentachloride into the acid chlorides: *e.g.*

$$\underset{\text{Succinic acid.}}{C^4H^6O^4} + PCl^5 = \underset{\text{Succinic anhydride.}}{C^4H^4O^3} + 2HCl + POCl^3.$$

$$\underset{\text{Succinic anhydride.}}{C^4H^4O^3} + PCl^5 = \underset{\text{Chloride of Succinyl.}}{C^4H^4O^2Cl^2} + POCl^3.$$

*Antimonic acid* and *boric acid* are also dehydrated by it, yielding the corresponding anhydrides, together with hydrochloric acid and oxychloride of phosphorus (Schiff, Ann. Ch. Pharm. cii. 111). Strong *nitric acid* acts very violently on the pentachloride, and when it is added to the latter by drops, hydrochloric acid escapes, and if the mixture be well cooled, a blood-red liquid is obtained which yields by distillation phosphoric oxychloride and yellow-red vapours, probably consisting of $NO^2Cl$. (Schiff.)

With strong *sulphuric acid*, the pentachloride first yields phosphoric oxychloride and chlorhydrosulphuric acid, and by prolonged action, chloride of sulphuryl, the so-called chlorosulphuric acid $(SO^2)''Cl^2$ (Williamson, Chem. Soc. Qu. J. vii. 185):

$$\underset{\text{Sulphuric acid.}}{SO^2\left\{\begin{matrix}HO\\HO\end{matrix}\right.} + PCl^5 = \underset{\text{Chlorhydrosulphuric acid.}}{SO^2\left\{\begin{matrix}Cl\\HO\end{matrix}\right.} + POCl^3 + HCl.$$

$$SO^2\left\{\begin{matrix}Cl\\HO\end{matrix}\right. + PCl^5 = SO^2Cl^2 + POCl^3 + HCl.$$

With *sulphuric anhydride*, the products are also phosphoric oxychloride and chloride of sulphuryl:

$$SO^3 + PCl^5 = POCl^3 + SO^2Cl^2.$$

With *sulphurous anhydride* in like manner chloride of thionyl, $(SO)''Cl^2$, is produced. On *phosphoric anhydride*, the pentachloride does not act in the cold, but when heated it acts easily, forming phosphoric oxychloride. Glacial and syrupy phosphoric acid are but slightly acted upon by it even when heated. (Schiff.)

9. Many *metallic oxides* and *salts* are readily decomposed by ignition in the vapour of phosphoric chloride, yielding phosphoric oxychloride and a metallic chloride or oxychloride. Such is the case with the *oxides of cadmium*, *manganese*, *cobalt*, and *chromium*, the last yielding a violet sublimate of chromic chloride. *Ferric oxide* and *alumina* yield slightly volatile sublimates consisting of the double chlorides $FeCl^3.PCl^5$ and $AlCl^3.PCl^5$, respectively. The minerals of the *spinel group*, when finely pulverised and treated in like manner are also decomposed with more or less facility, *chrome-iron*

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and *franklinite* yielding distillates containing ferric chloride, *spinel* yielding chloride of aluminium. *Titanate of iron* yields a brown sublimate and a distillate containing the chlorides of iron and titanium. Finely pulverised *silica* yields a fuming distillate which is decomposed by water, with formation of gelatinous silica; *felspar* and *garnet* yield similar distillates containing also chloride of aluminium. *Tungstic* and *molybdic anhydrides* are decomposed in a similar manner (Weber, Pogg. Ann. cvii. 375, Jahresh. 1859, p. 79). *Tungstic anhydride* heated with pentachloride of phosphorus yields a red-brown liquid, which when distilled gives off phosphoric oxychloride and leaves a substance, probably $(WO^2)''Cl^2$, which sublimes in yellow-red vapours. On *molybdic anhydride* the chloride acts more violently, the mixture giving off thick white and red vapours, and leaving a thick oily liquid which yields by distillation, first phosphoric oxychloride, then molybdic oxychloride, then, probably in consequence of a secondary reaction, a red woolly sublimate of molybdic dichloride (Schiff). *Arsenious anhydride* is easily decomposed by pentachloride of phosphorus, yielding phosphoric oxychloride and trichloride of arsenic; *arsenic anhydride* yields the same products, with evolution of chlorine (Hurtzig and Geuther, Jahresh. 1857, p. 186):

$$As^2O^3 \quad + \quad 3PCl^5 \quad = \quad 3POCl^3 \quad + \quad 2AsCl^3$$
$$As^2O^5 \quad + \quad 5PCl^5 \quad = \quad 5POCl^3 \quad + \quad 2AsCl^3 \quad + \quad Cl^4.$$

*Chloride of chromyl* (chlorochromic acid), $CrO^2Cl^2$, gently heated with phosphoric chloride yields a brown mass; at a stronger heat, phosphoric oxychloride and free chlorine are given off, and there remains a blue powder containing chromic and phosphoric chlorides, and converted at a red heat into violet chromic chloride:

$$2CrO^2Cl^2 \quad + \quad 4PCl^5 \quad = \quad 4POCl^3 \quad + \quad 2CrCl^3 \quad + \quad 3Cl^2$$

(Weber: see also Schiff, Jahresh. 1857, p. 107). *Boric anhydride* is but very slightly decomposed by ignition in the vapour of phosphoric chloride; *iodic anhydride* very easily (Weber). *Nitrate of silver* and *chlorate of potassium* are decomposed by phosphoric chloride at ordinary temperatures; *tungstate of iron* (wolfram), *sulphate of barium, phosphate of sodium* and other salts at a red heat (Weber). The decomposition of *chlorate of potassium* is represented by the equation:

$$KClO^3 \quad + \quad 3PCl^5 \quad = \quad 3POCl^3 \quad + \quad KCl \quad + \quad 3Cl^2.$$

Sometimes also a detonating gas (hypochlorous anhydride or chloric peroxide) is evolved, probably from the action of hydrochloric acid resulting from the presence of moisture (Baudrimont). According to Schiff (Ann. Ch. Pharm. cvi. 116) a dark yellow gas is given off, which may be heated without exploding, and when passed into dilute potash-solution, forms chloride, hypochlorite and chlorate of potassium.

10. *Metallic sulphides* heated in the vapour of pentachloride of phosphorus, are decomposed like the oxides, yielding metallic chloride and sulphochloride of phosphorus, $PSCl^3$, but generally with greater facility than the oxides, and sometimes with incandescence. *Iron pyrites, zinc-blende, sulphide of bismuth, realgar,* native *sulphide of antimony,* and *galena,* are easily and completely decomposed, the last with incandescence and formation of a brown-red product, probably a sulphochloride of lead; *arsenical pyrites, smaltine, cobalt-speiss,* and *red silver ore* are likewise easily decomposed. *Selenide of lead* yields chloride of lead and a reddish seleniferous liquid probably containing seleniochloride of phosphorus. Metallic *arsenides,* such as arsenical iron and copper-nickel, are but slowly attacked by pentachloride of phosphorus. (Weber, *loc cit.*)

11. *Sulphocyanate of potassium* gently heated with pentachloride of phosphorus yields gaseous chloride of cyanogen, sulphochloride of phosphorus, and chloride of potassium:

$$KCyS \quad + \quad PCl^5 \quad = \quad CyCl \quad + \quad KCl \quad + \quad PSCl^3.$$

A small quantity of chloride of sulphur is likewise formed. At a higher temperature larger quantities of chloride of sulphur distil over, together with trichloride of phosphorus and solid chloride of cyanogen; and a reddish-yellow residue is left, from which water extracts chloride of potassium, leaving sulphur and yellow decomposition-products of potassic sulphocyanate. The first reaction is probably:

$$6KCyS \quad + \quad 2PCl^5 \quad = \quad 2Cy^2Cl^2 \quad + \quad S^2Cl^2 \quad + \quad 2KCl \quad + \quad 2K^2S^2 \quad + \quad P^2,$$

the free phosphorus and the disulphide of potassium afterwards acting on fresh portions of the pentachloride, as follows:

$$P^2 \quad + \quad 3PCl^5 \quad = \quad 5PCl^3;$$
$$K^2S^2 \quad + \quad PCl^5 \quad = \quad PSCl^3 \quad + \quad 2KCl \quad + \quad S.$$

The yellow products above mentioned probably arise from another mode of decomposition of the sulphocyanate, produced simultaneously by the heat. (Schiff, Ann. Ch. Pharm. cvi. 116.)

With *phosphoretted hydrogen* pentachloride of phosphorus forms hydrochloric acid and trichloride of phosphorus, or free phosphorus, according to the proportions:

$$3PCl^5 \quad + \quad PH^3 \quad = \quad 3HCl \quad + \quad 4PCl^3$$
$$3PCl^5 \quad + \quad 5PH^3 \quad = \quad 15HCl \quad + \quad P^8.$$

12. Pentachloride of phosphorus rapidly absorbs *ammonia-gas*, forming sal-ammoniac, the so-called chlorophosphamide (p. 498), chloronitride of phosphorus, and perhaps other products:

$$PCl^5 \quad + \quad 4NH^3 \quad = \quad \underset{\text{Chlorophosphamide.}}{N^2H^4PCl^3} \quad + \quad 2NH^4Cl;$$

and

$$PCl^5 \quad + \quad 4NH^3 \quad = \quad \underset{\substack{\text{Chloronitride}\\\text{of phosphorus.}}}{PNCl^2} \quad + \quad 3NH^4Cl.$$

It was formerly supposed also that a compound of ammonia with the pentachloride was formed; but this does not appear to be the case. (See *Gmelin's Handbook*, ii. 482.)

13. *Amides* are decomposed by pentachloride of phosphorus in various ways. *Acetamide* acts very violently on the pentachloride, and on distilling the product, a considerable quantity of carbonaceous matter is left, while a compound of acetonitrile with trichloride of phosphorus, $C^2H^3N.PCl^3$, passes over (Henke, Ann. Ch. Pharm. cvi. 272). *Butyramide* yields in like manner the compound, $C^4H^7N.PCl^3$ (Henke); or according to Cahours (Compt. rend. xxv. 325), butyronitrile, oxychloride of phosphorus, and hydrochloric acid:

$$C^4H^9NO \quad + \quad PCl^5 \quad = \quad C^4H^7N \quad + \quad POCl^3 \quad + \quad 2HCl.$$

*Benzamide* yields in like manner, according to Henke, benzonitrile, $C^7H^5N$, oxychloride of phosphorus, and hydrochloric acid; according to Gerhardt, the first products of the reaction are oxychloride of phosphorus, and the compound $C^7H^7NCl^2$:

$$C^7H^7NO \quad + \quad PCl^5 \quad = \quad POCl^3 \quad + \quad C^7H^7NCl^2;$$

the latter being subsequently resolved into HCl and $C^7H^6NCl$, which when heated is further resolved into HCl and $C^7H^5N$ (benzonitrile). *Sulphophenylamide* (or *sulphiphenylamic acid*), $C^6H^7SO^2N$, heated with pentachloride of phosphorus yields sulphiphenylic chloronitride (Gerhardt's chloride of sulphophenylamidyl); according to the equation:

$$\underset{\substack{\text{Sulphiphenylamic}\\\text{acid.}}}{\left.\begin{matrix}H.C^6H^5\\(SO)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}} \quad + \quad PCl^5 \quad = \quad HCl \quad + \quad POCl^3 \quad + \quad \underset{\substack{\text{Sulphiphenylic}\\\text{chloronitride.}}}{\left.\begin{matrix}C^6H^4\\(SO)''\\H\end{matrix}\right\}\begin{matrix}N\\Cl.\end{matrix}}$$

*Benzosulphophenylamide* yields in like manner benzosulphiphenylic chloronitride:

$$\left.\begin{matrix}C^7H^5O\\C^6H^5\\(SO)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} \quad + \quad PCl^5 \quad = \quad HCl \quad + \quad POCl^3 \quad + \quad \left.\begin{matrix}C^7H^4O\\(SO)''\\C^6H^5\end{matrix}\right\}\begin{matrix}N\\Cl.\end{matrix}$$

(Gerhardt, Ann. Ch. Pharm. cviii. 214; compare Fittig, *ibid.* cvi. 277; Jahresb. 1858, pp. 314—320.)

### *Compounds of Pentachloride of Phosphorus with other Chlorides.*

These compounds are obtained either by direct combination of their proximate constituents, or by the action of various elementary bodies on pentachloride of phosphorus (p. 512). They are all less volatile than the latter, and may be freed from excess of it by heating for ten to twenty hours to 160°—180°, and further purified by sublimation at a higher temperature. They are all solid, volatile, fume in the air, and are decomposed by water, in some cases with rise of temperature. (Baudrimont, Compt. rend. lv. 361; Ann. Ch. Phys. [4] ii. 5.)

*Iodophosphoric chloride*, $PICl^6 = PCl^5.ICl$, is obtained by the action of iodine on the pentachloride; also by direct combination of its component chlorides, or of trichloride of phosphorus with trichloride of iodine; or by the action of trichloride of iodine on pentachloride of phosphorus:

$$PCl^5 \quad + \quad ICl^3 \quad = \quad PICl^6 \quad + \quad Cl^2.$$

It is orange-yellow, and may be obtained by distillation in beautiful needles which quickly absorb moisture and deliquesce to a corrosive liquid.

*Selenio-phosphoric chloride*, $P^2SeCl^{14} = 2PCl^5.SeCl^4$, obtained by direct combination is orange-yellow, boils at 220°, and acquires a transient red colour when heated till it volatilises.

*Alumino-phosphoric chloride*, $PAlCl^8 = PCl^5.AlCl^3$.—This compound, first obtained by Weber (Pogg. Ann. cvii. 375), is produced by direct combination, by heating finely divided alumina in the vapour of phosphoric chloride (Weber), or by the action of aluminium on that compound (Baudrimont). It is white, easily fusible, solidifies in the crystalline form on cooling; is much less volatile than either of the component chlorides (Weber), boils above 400° (Baudrimont). It is decomposed by phosphorus, with formation of trichloride of phosphorus; forms a dark red-brown mass when heated with sulphur; and when heated with chloride of potassium, gives off pentachloride of phosphorus, and is converted into chloride of aluminium and potassium.

*Ferrico-phosphoric chloride*, $PFeCl^8 = PCl^5.Fe'''Cl^3$, obtained by similar processes is brown, easily fusible, less volatile than either of the component chlorides (Weber); melts at 98° and boils above 280°. (Baudrimont.)

*Mercurico-phosphoric chloride*, $PHg^3Cl^{11} = PCl^5.3Hg''Cl^2$, forms easily fusible needles volatilising at about 200°, and decomposing when suddenly heated. (Baudrimont.)

*Platinico-phosphoric chloride*, $P^2PtCl^{14} = 2PCl^5.Pt^{iv}Cl^4$, obtained by the action of platinum on the pentachloride, is an amorphous ochre-brown mass, which volatilises with partial decomposition at temperatures above 300°. (Baudrimont.)

*Stannico-phosphoric chloride*, $PSnCl^9 = PCl^5.Sn^{iv}Cl^4$, produced by direct combination or by gently heating the compound, $2SCl^4.SnCl^4$ with trichloride of phosphorus in a current of dry hydrochloric acid gas:

$$2SCl^4.SnCl^4 \quad + \quad 3PCl^3 \quad = \quad PCl^5.Sn^{iv}Cl^4 \quad + \quad 2PCl^5 \quad + \quad S^2Cl^2;$$

also by heating the same compound with pentachloride of phosphorus in a stream of chlorine (Casselmann, Ann. Ch. Pharm. lxxxiii. 257; Jahresb. 1852, p. 393). It sublimes in brilliant colourless needle-shaped crystals, which soon crumble to an amorphous powder even in closed vessels (Casselmann). Melts at 220°, and volatilises with partial decomposition. (Baudrimont.)

**PHOSPHORUS, CHLORONITRIDE OF.** $P^3N^3Cl^6$. *Chlorophosphuret of Nitrogen.*—This compound was discovered by Wöhler and Liebig (Ann. Ch. Pharm. xi. 146), who assigned to it the formula $P^3N^2Cl^5$. It was further examined by Gladstone (Chem. Soc. Qu. J. iii. 135), whose analyses appeared to confirm this formula. Laurent however (Compt. chim. 1850, p. 387), suggested that the true formula of the compound was $PNCl^2$, derived from that of pentachloride of phosphorus by the substitution of 1 at. nitrogen for 3 at. hydrogen; and the correctness of this formula has been established by the recent analyses of Gladstone and Holmes (Chem. Soc. J. xvii. 225), who have however shown that it must be tripled in accordance with the observed vapour-density.

*Formation.*—By the action of pentachloride of phosphorus on ammonia, chloride of ammonium (Wöhler and Liebig), or chloride of dimercurammonium (white precipitate). (Gladstone and Holmes.)

*Preparation.*—1. Pentachloride of phosphorus is saturated with dry ammoniacal gas, and the white mass produced is distilled with water. The crystals which condense in the water contained in the receiver are then collected on a filter, washed, dried, and purified by solution in hot ether and recrystallisation (Wöhler and Liebig).—2. Pentachloride of phosphorus is placed at the closed end of a glass tube three feet long, and at a short distance from it, long pieces of sal-ammoniac are introduced, in such quantity that the tube may be half filled with them. The tube is then laid horizontally in a long furnace, similar to that used for organic analysis, and the sal-ammoniac heated till it begins to volatilise; a gentle heat is then applied to the chloride of phosphorus, so that its vapour may slowly pass over the sal-ammoniac, and be completely decomposed. A large quantity of hydrochloric acid gas is evolved, and the cool part of the tube becomes filled with crystals of chloronitride of phosphorus. This portion of the tube is broken off, and freed from sal-ammoniac by slightly washing it with water, and the compound is finally purified with ether (Wöhler and Liebig).—3. An intimate mixture of white precipitate and pentachloride of phosphorus is gently heated in a flask, whereupon a brisk action ensues, and chloronitride of phosphorus is formed, together with chlorophosphamide, mercuric chloride, and sal-ammoniac. The product is treated with water which dissolves out the two latter substances, and from the residue when dry the chloronitride may be extracted by means of ether, chloroform, or sulphide of carbon. This method is easier of execution than the preceding, but not more productive. (Gladstone and Holmes).

*Properties.*—Chloronitride of phosphorus separates from either of the solvents just mentioned in crystals belonging to the trimetric system.* Specific gravity = 1·98;

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* The paper by Gladstone and Holmes above referred to contains a full description of the form and optical properties of these crystals, by Professor W. H. Miller of Cambridge.

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small crystals or a film of the melted substance float however on water, doubtless from its inability to be wetted. Its specific refractive energy $\left(i.e.\ \frac{\text{refractive index} - 1}{\text{density}}\right)$ is by observation 0·316; by calculation from the specific refractive energies of its constituents (phosphorus 0·58, nitrogen 0·238, chlorine 0·242) it is 0·332 (Gladstone and Holmes). It melts at about 110° to a clear liquid which boils at 240°; it volatilises slowly at ordinary temperatures, and when heated gives off a dense vapour having a peculiar odour (Gladstone). It gives by analysis 25·96—26·44 per cent. phosphorus, 11·73 nitrogen, and 60·72—61·15 chlorine (Gladstone and Holmes), agreeing nearly with the formula $PNCl^2$, which requires 26·72 phosphorus, 12·07 nitrogen, and 61·21 chlorine. The vapour-density (mean of two determinations) = 12·21; whence the true formula of the compound is $P^3N^3Cl^6$, which, for a condensation to 2 volumes, gives for the calculated density the number 12·10.

Chloronitride of phosphorus is insoluble in water, which moreover does not easily wet it; easily soluble in *alcohol*, *ether*, *chloroform*, *sulphide of carbon*, *benzene*, *oil of turpentine* and other hydrocarbons. It is not decomposed by sublimation in hydrogen or sulphydric acid gas; or when heated with iodine (Gladstone). When ignited with *oxide of copper*, it yields nitrogen gas and nitric peroxide. Its vapour passed over red-hot *iron*, yields nitrogen gas, and a crystalline mass consisting of chloride and phosphide of iron (Wöhler and Liebig). Heated with *silver*, it yields chloride of silver, another silver-salt insoluble in nitric acid, and ammonia; it is decomposed in a similar manner by silver when dissolved in ether, the solution acquiring an acid reaction. Its alcoholic solution mixed with nitrate of silver, yields a precipitate of silver-chloride. According to Wöhler and Liebig, it is not attacked by sulphuric, hydrochloric, or nitric acid, even when heated; according to Gladstone, the crystallised substance is attacked only by hot fuming nitric acid, and more easily when dissolved in alcohol or ether.

When treated in alcoholic solution with *ammonia* or *potash*, it is immediately converted into pyrophosphodiamic acid (*q. v.*) (Gladstone and Holmes):

$$\underset{\substack{\text{Chloronitride}\\ \text{of phosphorus.}}}{2P^3N^3Cl^6} + 15H^2O = \underset{\substack{\text{Pyrophos-}\\ \text{phodiamic}\\ \text{acid.}}}{3P^2N^2H^6O^5} + 12HCl.$$

**PHOSPHORUS, CHLOROSULPHIDE OF.** See PHOSPHORUS, SULPHOCHLORIDE OF.

**PHOSPHORUS, CYANIDES OF.** Kemp found that cyanogen liquefied by strong pressure is capable of dissolving phosphorus; and Cenedella (Ann. Ch. Pharm. xviii. 70), by heating 5 grains of phosphorus with 20 grains of mercuric cyanide, obtained (unless a dangerous explosion took place) a white sublimate which had a very pungent odour of phosphorus and cyanogen, and dissolved in water with ebullition and separation of phosphorus, forming a solution of phosphoric acid, with traces of hydrocyanic acid (*Gmelin's Handbook*, viii. 147). Neither of these products, however, appears to have possessed any definite character, and the only known definite cyanide of phosphorus yet obtained is that which corresponds to the trichloride.

**Tricyanide of Phosphorus** or **Phosphorous Cyanide,** $PC^3N^3$ or $PCy^3$ (Hubner and Wehrhane, Ann. Ch. Pharm. cxxviii. 254; cxxxii. 277).—This compound is produced: 1. By heating cyanide of silver with trichloride of phosphorus in a sealed tube:

$$PCl^3 + 3AgCy = PCy^3 + 3AgCl.$$

2. Together with chloride of cyanogen and chloride of silver, by heating cyanide of silver with a solution of pentachloride of phosphorus in sulphide of carbon:

$$PCl^5 + 4AgCy = PCy^3 + CyCl + 4AgCl.$$

It is not formed by heating other metallic cyanides or hydrocyanic acid with trichloride of phosphorus, or by mixing phosphorus vapour with cyanogen gas or vapour of chloride of cyanogen.

*Preparation.*—Cyanide of silver is thoroughly moistened in a strong tube, which is kept cool, with trichloride of phosphorus; the tube is sealed and heated to 130°—140° for six or eight hours; the product is then warmed to drive off the excess of the trichloride; and the dry residue is heated to 130°—140°, or at most to 180°, in a retort having its beak directed upwards (best in a slow stream of carbonic anhydride) till it sublimes. The retort is then closed air-tight and left to cool, and the crystals of phosphorous cyanide are removed from the neck by a glass rod, 20 to 25 grammes of silver-cyanide yield 4·5 to 4·8 grammes cyanide of phosphorus.

*Properties.*—Tricyanide of phosphorus forms long white needles or thick plates, which take fire even on being touched with a warm glass rod, and gradually disintegrate

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in contact with moist air, with separation of phosphorus, formation of phosphorous acid and evolution of hydrocyanic acid. It melts between 200° and 203°, and remains liquid for some time after fusion, but solidifies on being touched with a solid body. It boils at a few degrees above its melting point. It is but slightly soluble in *ether, chloroform, sulphide of carbon* or *trichloride of phosphorus*, more easily however near its melting point. In contact with *water*, it is rapidly decomposed, yielding hydrocyanic and phosphorous acids. With *ethylic* or *amylic alcohol*, it produces the corresponding phosphorous ether, together with a large quantity of hydrocyanic acid and a fetid body, the same apparently as that which is formed in the preparation of cyanide of ethyl (ii. 211). *Acetic acid* acts on phosphorous cyanide with great violence, often producing separation of carbon. With *valerianic acid* it forms hydrocyanic acid, phosphorous acid and an oily body exhibiting the reactions of cyanide of valeryl. *Chloride of acetyl* acts upon it at 100°, but the reaction does not yield any easily separable products. It is not acted upon by dry *ammonia gas* at ordinary temperatures, but when heated in that gas, it is converted into a black mass insoluble in water.

**PHOSPHORUS, DETECTION AND ESTIMATION OF.** Phosphorus, as already observed, occurs in nature most frequently in the form of a phosphate. The reactions of these salts, and the methods of estimating the phosphoric acid or the phosphorus contained in them will be given hereafter (see PHOSPHORUS, OXYGEN-ACIDS OF).

In the lower oxygen-compounds of phosphorus, namely the phosphites and hypophosphites, the phosphorus is determined by converting them into phosphates by oxidation with nitric acid, or better with hydrochloric acid and chlorate of potassium, or by their reducing action on salts of gold or mercury.

The chlorides of phosphorus are analysed by decomposing them with water or with alkaline solutions, whereby they are converted into hydrochloric acid, and phosphorous or phosphoric acid, according as the compound operated on is a tri- or pentachloride. In the latter case, the phosphorus may be immediately precipitated as ammonio-magnesian phosphate; in the former it must first be brought to the state of phosphoric acid by oxidation with nitric acid. The chlorine may be determined by precipitation with nitrate of silver. The same method serves for the analysis of the bromides, iodides, and cyanide of phosphorus.

The sulphides of phosphorus may be decomposed by fusion with nitre and carbonate of sodium, or by treatment with hydrochloric acid and chlorate of potassium. In either case, the phosphorus is converted into phosphoric acid, the sulphur into sulphuric acid, and the former may be precipitated by solution of magnesia and ammonia, the latter as a barium-salt.

The same method is applicable to the selenides of phosphorus.

The nitrogen-compounds of phosphorus, viz. the phosphamides and phosphamic acids, are decomposed by the action of alkalis, the phosphorus being thereby converted into a salt of phosphoric acid. Chloronitride of phosphorus is decomposed by treating its alcoholic solution with ammonia, whereby it is converted into chloride and pyrophosphodiamate of ammonium (p. 517). The chlorine is then thrown down by nitrate of silver in presence of nitric acid, and the pyrophosphodiamic acid is converted into phosphoric acid by boiling its solution for some time with hydrochloric acid. (Gladstone and Holmes.)

The phosphorus in organic compounds is converted into phosphoric acid, either by fusion with nitre and carbonate of sodium, or by Carius's method of heating with nitric acid in sealed tubes (see ANALYSIS, ORGANIC, i. 248). Many animal and vegetable substances contain phosphorus, partly as phosphoric acid, partly in combination with the organic matter. To estimate the quantities of phosphorus existing in these two states, a known weight of the compound is boiled with hydrochloric acid, which dissolves the phosphate present, and possibly another portion or even the whole of the compound, though that is seldom the case. The liquid is then filtered and the phosphoric acid precipitated as ammonio-magnesian phosphate. Another portion of the compound is oxidised by one of the methods above mentioned, and the phosphoric acid determined in like manner. If the quantities of phosphoric acid obtained in the two cases are equal, it may be concluded that all the phosphorus in the original compound was in the form of phosphoric acid; if on the other hand the oxidised portion is found to yield a larger quantity of phosphoric acid, the quantity of phosphorus existing in the non-oxidised condition may be calculated from the difference.

Gaseous compounds of phosphorus and hydrogen are analysed by passing them in the perfectly dry state over a weighed quantity of sulphide or chloride of copper, nickel, cobalt, or iron, of known composition, kept at a moderate heat in a bulb-tube. The metal is thereby completely converted into phosphide, and the sulphur or chlorine passes off as sulphydric or hydrochloric acid. The bulb-tube containing the metallic chloride or sulphide is weighed, first empty, then with the chloride or sulphide in it,

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and lastly at the completion of the experiment. The composition of the chloride or sulphide used being previously known, the quantity of metal contained in it is also known and the excess of weight of the metallic phosphide over this gives the quantity of phosphorus in the gas. To determine the quantity of hydrogen that was in combination with it, the sulphur or chlorine that has united with this hydrogen must be collected and estimated. When a sulphide is used, the sulphydric acid produced may be passed into a solution of lead or copper, the precipitated sulphide oxidised by nitric acid, and the sulphur precipitated as sulphate of barium (see SULPHUR). If the original metallic compound was a chloride, the hydrochloric acid which passes off is passed into dilute ammonia; the resulting solution neutralised with nitric acid, and the chlorine precipitated by nitrate of silver. The quantity of sulphur or chlorine which has been expelled as a hydrogen-compound being thus known, the quantity of hydrogen which has entered into combination with it, which is the same as that originally combined with the phosphorus, is easily calculated. This method gives trustworthy results even when the phosphoretted hydrogen gas is mixed with a considerable quantity of free hydrogen; for the sulphides of the metals above mentioned are not decomposed by free hydrogen, even at high temperatures; neither are their chlorides decomposed by that gas at the temperature required for the decomposition of the phosphoretted hydrogen, especially in presence of an excess of the latter. The sulphides, however, give for the most part more exact results than the chlorides.

To determine the total amount of hydrogen as well as of phosphorus in a mixture of phosphoretted hydrogen and free hydrogen, the gas, after being thoroughly dried, is passed, through a tube containing very finely divided metallic copper heated to redness. The phosphorus then unites with the copper, and the hydrogen thus liberated, together with that originally existing in the free state, passes into a second tube containing oxide of copper likewise heated to redness, whereby the hydrogen is converted into vapour of water, which passes on and is collected in a third tube containing dry chloride of calcium. The increase of weight of the first tube, after the experiment gives the quantity of phosphorus, and the increase of weight of the third tube gives the quantity of water formed, whence the total quantity of hydrogen is determined. In this manner the relative quantities of free hydrogen and phosphoretted hydrogen, $PH^3$, in the gas may be found. For other methods see H. Rose. (*Traité de Chimie Analytique*, ii. 1172.)

**Metallic phosphides** are analysed by dissolving them in nitric acid, nitro-muriatic acid, or a mixture of hydrochloric acid and chlorate of potassium. The phosphorus is thereby completely converted into phosphoric acid, the metal being for the most part dissolved at the same time. The metal may then be precipitated from the solution by sulphydric acid or sulphide of ammonium (after the excess of nitric acid has been driven off or nearly neutralised), and from the filtrate the phosphoric acid may be precipitated as ammonio-magnesian phosphate. If pure nitric acid has been used to dissolve the compound, the solution may be evaporated to dryness, the calcined residue decomposed by fusion with an alkaline carbonate, the fused mass digested with water, and the phosphoric acid precipitated from the filtered alkaline solution as above. The phosphide may also be decomposed at once by fusion with four or five times its weight of a mixture of nitre and alkaline carbonate.

Most metallic phosphides are insoluble in hydrochloric acid, even when heated. Nevertheless when a very small quantity of phosphorus is associated with a large quantity of iron, as in many kinds of pig-iron, the whole dissolves in hydrochloric or dilute sulphuric acid, the phosphorus passing into solution as phosphoric acid. (For the methods of estimating phosphorus in pig-iron, see iii. 373.)

*Testing for free Phosphorus.*—The properties and reactions of phosphorus in the free state have been already described. Ordinary phosphorus is especially distinguished by its ready inflammability, the bright flame and dense white fumes of phosphoric anhydride produced by its rapid combustion, and by the peculiar odour and luminosity in the dark resulting from its slow combustion at ordinary temperatures. Oils and fatty substances mixed with finely divided phosphorus likewise shine in the dark with a greenish-white light. Small quantities of phosphorus in the state of vapour or mechanically suspended particles, impart a peculiar greenish colour to the flame of hydrogen and other combustible gases.

When the quantity of free phosphorus mixed with any substance is too small to produce luminosity, it might be detected by oxidising it to phosphoric acid by means of nitric acid or hydrochloric acid and chlorate of potassium, and testing for phosphoric acid by the usual methods. But when phosphorus has to be searched for in cases of poisoning, this method is of no value: for phosphoric acid is contained in most of the tissues and fluids of the animal body, and in the majority of substances which are used as food. To obtain the reactions of this acid in the substance under examination, affords therefore no proof that phosphorus has been administered; the only satisfactory

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evidence of such administration is to produce the phosphorus in the free state, or at least to exhibit its luminosity.

The process generally used for this purpose is that devised by Mitscherlich (J. pr. Chem. lxvi. 238; Jahresb. 1855, p. 779). The suspected substance is distilled with water and sulphuric acid in a flask fitted up with a delivery-tube bent twice at right angles and dipping into a receiver containing water, which must be kept cool: for gases and vapours containing free phosphorus do not exhibit luminosity when their temperature is raised above a certain point. The distillation is performed in the dark. As soon as the vapours arrive in the cool part of the tube, a continual phosphorescent light is observed therein, generally in the form of a shining ring; at the same time globules of phosphorus are deposited in the receiver. In this manner 1 pt. of phosphorus may be detected in 100,000 pts. of substance. The luminosity of phosphorus is however prevented by the presence of certain volatile substances, among others by ether, alcohol, oil of turpentine and ammonia. Ether and alcohol being very volatile, quickly pass off at the commencement of the distillation, so that their disturbing influence is soon eliminated; oil of turpentine, on the contrary, would prevent the phosphorescent appearance during the whole of the distillation; but this substance is not likely to be present in matters which become the subject of medico-legal investigations. Ammonia if present will be retained by the sulphuric acid in the flask.

Scherer (Ann. Ch. Pharm. cxii. 214), modifies the preceding process by filling the apparatus before commencing the distillation, with carbonic acid gas, which is easily effected by throwing a few lumps of chalk into the flask containing the acid liquid. The phosphorescence in the tube is then seen just as before (the oxygen being of course not completely expelled), but the conversion of the phosphorus into phosphorous acid is in a great measure prevented, so that a larger portion of it is collected in the free state. The water in the condensing vessel shines strongly when agitated in the dark, and gives a blackish precipitate with nitrate of silver.

Small quantities of phosphorus diffused through organic matter may be collected and approximately estimated by means of *sulphur*. The substance under examination is mixed in a tubulated retort with dilute sulphuric acid, a few pieces of sulphur are added, and the whole is distilled for about half an hour. The distillate frequently contains small quantities of phosphorous and phosphoric acids formed by oxidation of the phosphorus vapours. It may be treated with nitric acid in order to convert the whole of the phosphorus into phosphoric acid, and the quantity then determined by precipitation as ammonio-magnesian phosphate.

The residue in the retort is removed after cooling and the lumps of sulphur are picked out and washed. They contain all the free phosphorus in the original substance which has not passed over into the distillate. If the phosphorus is in excess, its combination with sulphur is liquid even after complete cooling; in the contrary case, the compound when cold is a soft, plastic, crystalline mass. If the sulphur contains only 2 per cent. of phosphorus, it may still fume on exposure to the air even after drying, and turns black when moistened with silver-solution; the latter effect is produced indeed even when the proportion of phosphorus in the sulphur does not exceed 1 per cent. The phosphorised sulphur also shines in the dark when heated to 100°. By digesting it with nitric acid, the phosphorus contained in it is easily converted into phosphoric acid, which may then be precipitated as above. (Lipowitz, Pogg. Ann. xc. 600; Jahresb. 1853, p. 641.)

Dusart (Compt. rend. xliii. 1126; Jahresb. 1856, p. 724) employs for the detection of small quantities of phosphorus, the production of phosphoretted hydrogen which takes place when the substance containing the phosphorus is exposed to the action of *nascent hydrogen*. The substance is introduced into a generating vessel containing zinc and dilute sulphuric acid, and fitted up like Marsh's apparatus for the detection of arsenic (i. 362). If phosphorus is present, the evolved gas will contain phosphoretted hydrogen and will burn with an emerald-green flame. The green colour disappears however as soon as the end of the tube becomes hot; but on holding a piece of porcelain in the flame, the green colour again becomes visible where the flame is in contact with the cold surface. If the end of the tube be curved and made to dip under mercury, with only the very extremity projecting above the surface, so as to keep it constantly cool, the gas will give a continuous emerald-green flame, surrounded by an outer pale blue envelope. Blondlot (Compt. rend. lii. 1197; Jahresb. 1861, p. 821) recommends the use of a fine platinum jet, in order to avoid the yellow colouring of the flame produced by the sodium in glass. As commercial zinc often contains phosphorus, and it is therefore necessary to use pure distilled zinc which yields but a slow stream of gas, he collects the gas, before igniting it, in an apparatus somewhat like a Döbereiner's platinum-lamp. The green colouring of the flame is more or less interfered with by the presence of organic matters, namely, alcohol, ether, volatile oils and soluble animal substances. In such cases the gas may be passed through a dilute solution of

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silver-nitrate, and the resulting precipitate treated in another hydrogen apparatus as above. By this means also the presence of phosphorus may be detected after gradual oxidation, and when it no longer exhibits luminosity in Mitscherlich's apparatus.

Fresenius and Neubauer (Analyt. Zeitschr. p. 336) object to the preceding process, that the large quantity of zinc-salt produced in the liquid interferes with the subsequent examination for metallic poisons; they therefore prefer driving out the phosphorus by a stream of carbonic anhydride. For this purpose the flask containing the suspected substance and the dilute sulphuric acid is connected with an apparatus for generating carbonic anhydride, and is also provided with a delivery-tube connected with a U-tube containing a neutral solution of nitrate of silver. The whole apparatus is first filled with carbonic anhydride, the flask then heated to 60° or 70° for several hours, the stream of gas being kept up all the time; and the precipitate formed in the silver-solution is collected, carefully washed, and treated in a hydrogen apparatus as above.

Scherer (Ann. Ch. Pharm. cxii. 224) employs for the detection of phosphorus a process depending upon its volatility and its reaction with silver-solution. A piece of thin filtering paper moistened with nitrate of silver, and suspended over a slightly warmed liquid containing free phosphorus, soon becomes blackened, the silver being reduced by the phosphorus. As however, the blackening might proceed from sulphydric acid evolved from the liquid, it is necessary in the first instance to suspend, in the flask containing the acidulated liquid under examination, a strip of paper moistened with solution of nitroprussiate of sodium or acetate of lead; if no blueing of the paper takes place in the one case or blackening in the other it may be inferred that the liquid does not give off sulphydric acid, and the blackening of the paper moistened with silver-solution may then be attributed to the presence of phosphorus. If a considerable quantity of silver-phosphide is formed, it may be oxidised by chlorine-water, and the resulting solution tested for phosphoric acid with a magnesium-salt or with molybdate of ammonium. It is necessary, however, to make a comparative experiment with an equal portion of the clean paper, as phosphoric acid may be already present in it. Fresenius and Neubauer (*loc. cit.*) observe also that the blackening of the paper may arise from certain acids generated in the process of putrefaction, and would therefore in some cases give uncertain indications.

For the more certain detection of phosphorus in all cases in which it is not already wholly converted into phosphoric acid, Fresenius and Neubauer recommend the following series of operations:—1. It must be ascertained whether the substance shines in the dark when agitated. A small portion is then to be tested by Scherer's method with strips of paper moistened, the one with silver- the other with lead-solution; if only the former is blackened, phosphorus is most probably present.—2. A portion of the suspected substance is treated by Mitscherlich's process (p. 520). If no phosphorescence is observed in the tube, and no free phosphorus collects in the distillate, the latter is to be tested in the hydrogen apparatus (p. 520).—3. If these experiments give only negative results, the substance is to be heated in a stream of carbonic anhydride, the gas passed through silver-solution above described, and the resulting precipitate, if any, treated in the hydrogen apparatus.—4. The *quantity* of phosphorus present may be determined in another portion of the substance by Mitscherlich's process as modified by Scherer (p. 520). The flask which serves as a receiver is to be connected air-tight, on the one side with the condensing-tube which dips into the water in the receiver, on the other side with a U-tube containing neutral silver-solution; the distillation is kept up for 2½ hours. If any globules of phosphorus collect in the receiver, they may be collected and weighed. The liquid distillate is then to be mixed with the contents of the U-tube, oxidised with chlorine-water, and the resulting phosphoric acid determined in the usual way.—5. Phosphorised substances which have been exposed to the air for some time may still contain part of the phosphorus in the form of phosphorous acid. In this case the residues, which in the preceding experiments have given only negative results, are to be treated as above described in the hydrogen apparatus, the evolution of hydrogen being kept up for several hours, while the apparatus is warmed in the water-bath, the evolved gas passed through a U-tube containing silver-solution, and the precipitate examined for phosphorus as above.

*Atomic Weight of Phosphorus.*—The atomic weight of this element was correctly determined by Berzelius in 1816 (Schw. J. vii. 43). By decomposing trichloride of gold with phosphorus, he found in one experiment that 0·829 grm. phosphorus threw down 8·714 grm. gold, and in another 0·754 grm. phosphorus threw down 7·93 grm. gold: hence from the equation $5AuCl^3 + P^3 = 3PCl^5 + Au^5$, taking the atomic weight of gold at 196, the mean of the two experiments gives:

$$P = \frac{1·583 \times 196 \times 5}{16·644 \times 3} = 31·04.$$

A similar experiment with nitrate of silver gave $P = 31·34$.

Pelouze, in 1847 (Compt. rend. xx. 1047), by decomposing an acid solution of silver-nitrate with trichloride of phosphorus, obtained a higher number, viz. 32; but the result first obtained by Berzelius has been fully confirmed by the more recent and very careful experiments of Schrötter in 1853 (Ann. Ch. Pharm. lxxx. 202), and of Dumas in 1860 (*ibid.* cxiii. 28).

Schrötter burnt weighed quantities of amorphous phosphorus in a stream of dry oxygen, the apparatus being so arranged that no phosphoric anhydride could be lost. In ten experiments thus made, 100 pts. phosphorus yielded from 229·30 to 228·78 pts. phosphoric anhydride, $P^2O^5$—mean 228·92; whence the proportion $P^2 : P^2 + 80 = 100 : 228{\cdot}92$ gives $P = 31{\cdot}03$.—Dumas, by decomposing very pure trichloride of phosphorus with a standard solution of silver-nitrate ($2PCl^3 + 3Ag^2O = P^2O^3 + 6AgCl$), obtained in five experiments the following results:—

| | | | | |
|---|---|---|---|---|
| 1·787 | grm. $PCl^3$ required | 4·208 | silver : therefore P = | 31·01 |
| 1·466 | ,, | 3·454 | ,, | 31·00 |
| 2·056 | ,, | 4·844 | ,, | 31·00 |
| 2·925 | ,, | 6·890 | ,, | 31·04 |
| 3·220 | ,, | 7·582 | ,, | 31·09 |

From all these results, the number 31 is now universally adopted as the atomic weight of phosphorus.

**PHOSPHORUS, FLUORIDE OF.** $PF^3$. A very volatile compound first obtained by Davy, and further examined by Dumas. It is prepared by distilling fluoride of lead or mercury with phosphorus, a phosphide of the metal then remaining, while fluoride of phosphorus distils over. It is a colourless inflammable liquid, which fumes strongly in the air, and is said to yield by combustion, phosphoric anhydride and fluorine. Water converts it into phosphorous and hydrofluoric acids.

**PHOSPHORUS, HYDRATE OF?** The white crust which forms on the surface of phosphorus immersed in water, is said by Pelouze to be a hydrate, $P^2.H^2O$; but it appears rather to be an allotropic modification of phosphorus (p. 503).

**PHOSPHORUS, HYDRIDES OF.** (See HYDROGEN, PHOSPHIDES OF, iii. 199.)

**PHOSPHORUS, IODIDES OF.** Two of these compounds are known—namely, the tri-iodide, analogous to the trichloride and tribromide; and the di-iodide, of which there is no chlorine or bromine representative. The di- and tri-iodide are prepared by dissolving phosphorus and iodine together in sulphide of carbon, and cooling the liquid artificially till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallise out, mixed with excess either of iodine or of phosphorus.

The *di-iodide*, $PI^2$, melts at 110°, forming a red liquid, which condenses to a light red solid. It is soluble in sulphide of carbon, and is deposited therefrom in flattened prismatic orange-coloured crystals. It is decomposed by water into hydriodic and phosphorous acids, with a deposit of yellow flakes. With *glycerin* it yields tritylene-gas, a distillate of water, and iodo-tritylene (iodide of allyl), and a residue of oxygen-acids of phosphorus together with free iodine, undecomposed glycerin, and a trace of red phosphorus. The principal part of the reaction appears to take place thus:

$$\underset{\text{Glycerin.}}{C^3H^8O^3} + PI^2 = \underset{\substack{\text{Iodide of}\\\text{allyl.}}}{C^3H^5I} + \underset{\substack{\text{Phosphor-}\\\text{ous acid.}}}{PH^3O^3} + I.$$

This iodide appears also to be formed on dissolving a small quantity of iodine in melted phosphorus and heating the mixture to about 125°, and to be subsequently decomposed, yielding amorphous phosphorus (p. 504). When phosphorus is melted in a flask filled with carbonic anhydride, iodine projected through an upright tube reaching nearly to the phosphorus, and a gentle heat applied, violent action takes place attended with development of intense heat. The product is a very hard semi-metallic black mass of amorphous phosphorus, yielding a red powder. The first stage of the reaction is the formation of an iodide of phosphorus, probably the di-iodide, in which the phosphorus exists in the amorphous modification. This compound is then decomposed, with separation of amorphous phosphorus and formation of a more volatile iodine-product, which reacts upon a second portion of phosphorus, reproducing the first decomposible iodide, and so on continually. In this manner a small quantity of iodine can convert an almost indefinitely large quantity of phosphorus into the amorphous modification. (Brodie, Chem. Soc. J. v. 289.)

*Tri-iodide of Phosphorus* or *Phosphorous Iodide*, $PI^3$, melts at 55°, and crystallises in well-defined prisms on cooling. It is very soluble in sulphide of carbon, and is deposited therefrom in dark-red hexagonal plates. It absorbs moisture from the atmosphere, forming hydriodic and phosphorous acids.

*Penta-iodide.* $PI^5$? Gay-Lussac, by heating 1 pt. of phosphorus with 20 to 24 pts. of iodine, obtained a black substance which melted at 40°, and was said to be decomposed by water into hydrochloric and phosphoric acids. This decomposition, and the proportions of iodine and phosphorus used in the preparation, would indicate that the compound is a penta-iodide, but it requires re-examination. (*Berzelius' Lehrbuch.*)

**PHOSPHORUS, NITRIDE OF.** The compound obtained by saturating trichloride of phosphorus with ammonia-gas and heating the product in a current of carbonic anhydride (H. Rose), or by passing the vapour of trichloride or pentachloride of phosphorus over heated sal-ammoniac (Wöhler and Liebig), was originally supposed to be a di-nitride of phosphorus, $PN^2$; but, according to Gerhardt, the product obtained by either of these processes contains hydrogen, and consists of phospham, $PHN^2$ (p. 497).

**PHOSPHORUS, OXIDES AND OXYGEN-ACIDS OF.** Three anhydrous oxides of phosphorus are known, namely—

| | |
|---|---|
| Suboxide of Phosphorus | $P^4O$ |
| Trioxide of Phosphorus, Phosphorous Oxide, or Anhydride | $P^2O^3 = \left.\begin{matrix}P'''\\P'''\end{matrix}\right\}O^3$ |
| Pentoxide of Phosphorus, Phosphoric Oxide, or Anhydride | $P^2O^5 = \left.\begin{matrix}P^v\\P^v\end{matrix}\right\}O^5$. |

The second and third of these oxides, which are analogous in composition to the chlorides and bromides, unite with water, forming phosphorous acid, $P^2O^3.3H^2O$ or $PH^3O^3$, and phosphoric acid, $P^2O^5.3H^2O$ or $PH^3O^4$. There is also another acid of phosphorus, viz. hypophosphorous acid, $PH^3O^2$, to which there is no corresponding anhydride. The protoxide of phosphine, $PH^3O$, is not known; but it is represented by the compounds $PCl^3O$ and $P(C^2H^5)^3O$.

The three acids just mentioned all contain 3 atoms of hydrogen, having in fact the composition of oxides of phosphine, $PH^3$; nevertheless they have not the same basicity, phosphoric acid alone being properly tribasic, that is, capable of exchanging all its three hydrogen-atoms for an equivalent quantity of metal, whereas phosphorous acid is dibasic, and hypophosphorous acid monobasic; thus:

| | |
|---|---|
| Hypophosphorous acid | $PH^3O^2 = H.PH^2O^2$ |
| Phosphorous acid | $PH^3O^3 = H^2.PHO^3$ |
| Phosphoric acid | $PH^3O^4 = H^3.PO^4$. |

There are also certain acids resulting from the dehydration of phosphoric acid—viz., pyrophosphoric acid, $H^4P^2O^7 = 2H^3PO^4 - H^2O$, metaphosphoric acid, $HPO^3 = H^3PO^4 - 2H^2O$, and several polymeric modifications of the latter, which will be noticed hereafter.

The relations of hypophosphorous, phosphorous, and phosphoric acids to one another and to phosphoretted hydrogen or phosphine are remarkable. Hypophosphorous acid, $H^3PO^2$, has not been obtained directly from phosphine; but, on the other hand, it yields phosphine by deoxidation, as for example when zinc is dissolved in the aqueous acid, either alone or mixed with sulphuric acid. The solution of hypophosphorous acid when exposed to the air is gradually converted into phosphorous acid, and finally into phosphoric acid. When heated by itself, hypophosphorous acid is resolved into phosphoric acid and phosphine: $2H^3PO^2 = H^3PO^4 + H^3P$.

Phosphorous acid results from the slow oxidation of phosphine. Conversely, when phosphorous acid is acted upon by zinc, or zinc and sulphuric acid, it is deoxidised to phosphine. Phosphorous acid, when exposed to the air, takes up oxygen, and is converted into phosphoric acid. When heated by itself, it breaks up into phosphoric acid and phosphine: $4H^3PO^3 = 3H^3PO^4 + H^3P$.

Phosphoric acid, $H^3PO^4$, results from the combustion of phosphine in air or oxygen; also from the decomposition by heat and direct oxidation of hypophosphorous and phosphorous acids. It is much more stable than either of the other two acids, but, like them, may be made to yield phosphine by deoxidation, namely when treated with potassium or sodium.

**Suboxide of Phosphorus.** $P^4O$. When phosphorus is burnt in air or oxygen, a solid orange-coloured matter is left behind, which slowly deliquesces, forming phosphorous acid. A similar substance is formed in larger quantity by passing a current of oxygen-gas through phosphorus melted under hot water. This body, when dried by pressure between filter-paper and freed from phosphorus by treatment with sulphide of carbon, leaves a dark-red residue which has been described as a definite oxide of phosphorus, but is now generally regarded as amorphous phosphorus contaminated with a little phosphoric acid. Leverrier (Ann. Ch. Pharm. xxvii. 167) noticed that when small pieces of phosphorus covered by a layer of trichloride of phosphorus were exposed to the air, a peculiar yellow substance, soluble in water, was produced. At an increased temperature the solution decomposed into phosphoric acid, and a flocculent substance, which, when dried in a vacuum over oil of vitriol, left a canary-yellow powder, the composition of which was represented by the formula $P^4O$. It could be preserved for any length of time in dry air. When heated it acquired a bright-red colour, but was unaffected in composition by a temperature of 300°; when more strongly heated it took fire. (See *Gmelin's Handbook*, ii. 110.)

### Hypophosphorous Acid and Salts.

HYPOPHOSPHOROUS ACID, $H^3PO^2$, is obtained by decomposing the barium-salt with an equivalent quantity of sulphuric acid, or the lead-salt with sulphydric acid, and evaporating the filtrate:

$$Ba''P^2H^4O^4 \quad + \quad H^2SO^4 \quad = \quad 2H^3PO^2 \quad + \quad Ba''SO^4$$
$$Pb''P^2H^4O^4 \quad + \quad H^2S \quad = \quad 2H^3PO^2 \quad + \quad Ba''S$$

It is a viscid uncrystallisable liquid, having a strong acid reaction. When heated, it is resolved into phosphoric acid and phosphine: $2H^3PO^2 = H^3PO^4 + H^3P$. Its aqueous solution is a colourless mobile liquid, which when exposed to the air, is oxidised to phosphorous and phosphoric acids. It reduces the salts of *silver* and *gold*, with precipitation of the respective metals. It also reduces solution of *mercuric chloride* with precipitation of calomel or of metallic mercury, according to the proportion of acid used and the temperature at which the reaction takes place. By *zinc* and sulphuric acid it is deoxidised to phosphine, $PH^3$, which is given off as gas. Heated with solution of *cupric sulphate* to 55°—60°, it forms a precipitate of cuprous hydride, CuH (Wurtz: see COPPER, ii. 66). This reaction distinguishes hypophosphorous from phosphorous acid, which it otherwise much resembles.

**Hypophosphites.**—$MPH^2O^2$, or $M''P^2H^4O^4$, according to the atomicity of the metal. These salts are prepared: 1. By neutralising the acid with bases.—2. By boiling phosphorus in alkaline solutions; thus with lime or baryta-water:

$$3Ca''H^2O^2 + P^8 + 6H^2O = 3Ca''H^4P^2O^4 + 2PH^3.$$

The hypophosphite of calcium or barium may be crystallised out by cautious evaporation. When phosphorus is boiled with an aqueous solution of potassic hydrate a similar reaction takes place, but much phosphate of potassium is likewise formed; such is not the case, however, when an alcoholic solution of potash is employed. Hypophosphites are also formed, together with phosphine, by the action of water on the impure phosphides of barium, calcium, and strontium, obtained by heating phosphorus with the anhydrous earths (i. 507, 719). The reaction appears to be much the same as when a mixture of lime, &c. and phosphorus is acted upon by water.—3. By double decomposition: the magnesium-salt, for example, is prepared by boiling hypophosphite of calcium with oxalate of magnesium.

The hypophosphites are crystallisable salts soluble in water, and many of them also in alcohol. Some contain water of crystallisation. When dry they are permanent in the air; but their solutions are gradually oxidised on exposure, especially at the boiling heat. When boiled in alkaline liquids, they are decomposed into phosphate and hydrogen: *e. g.*—

$$KPH^2O^2 + 2KHO = K^3PO^4 + H^4.$$

The dry salts decompose when heated, giving off phosphoretted hydrogen (hence they are very inflammable), and leaving a residue of pyrophosphate: *e. g.*—

$$2Ba''P^2H^4O^4 = 2PH^3 + H^2O + \overset{''}{Ba}{}^2P^2O^7.$$

The hypophosphites, like the aqueous acid, act as powerful reducing agents, especially with aid of heat. With nitrate of silver they form a white precipitate, which quickly turns brown and is converted into metallic silver.

*Quantitative Analysis of Hypophosphites.*—The quantity of phosphorus in a hypophosphite may be determined by converting it into a phosphate by oxidation with nitric acid: the oxidation is not, however, complete till the solution has been evaporated down nearly to a syrup, and has attained a high temperature. The calcined residue consists of a metaphosphate, $MPO^3$ or $M''P^2O^6$, from the weight of which, if only one base is present, the amount of phosphorus (or the equivalent quantity of hypophosphorous acid, $H^3PO^2$, if required) may at once be calculated. If more than one base is present, the residual salt must be analysed, by the methods hereafter to be described for phosphates, and the quantity of phosphorus therein determined.

If a hypophosphite contains water of crystallisation, its amount must be determined by comparing the original weight of the hypophosphite with that which corresponds with the weight of metaphosphate actually obtained; or the metaphosphate may be

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analysed, the quantities of acid and base in the hypophosphite thence determined, and the water estimated by difference.

As all hypophosphites are soluble in water, the bases may be precipitated from their solutions by the ordinary reagents, sulphydric acid, sulphide of ammonium, alkalis &c.; the hypophosphorous acid may then be converted into phosphoric acid by oxidation with nitric acid, or better, with hydrochloric acid and chlorate of potassium; and the phosphoric acid precipitated as ammonio-magnesian phosphate.

The quantity of phosphorus in an aqueous solution of hypophosphorous acid containing no fixed base, and no other acid except nitric acid, is easily determined by adding to the solution a known weight of recently calcined oxide of lead, then adding nitric acid, evaporating to dryness, and calcining. The residue consists of a mixture of oxide and phosphate of lead, and on deducting the original weight of lead-oxide added, the difference gives the weight of phosphoric anhydride in the residue—whence the phosphorus may be calculated.

Lastly, hypophosphorous acid may be estimated by its reducing action on mercuric chloride, 1 at. of the acid precipitating 4 at. mercurous chloride, according to the equation:

$$H^3PO^2 + 4Hg''Cl^2 + 2H^2O = 4HgCl + H^3PO^4 + 4HCl.$$

The aqueous solution of the acid or of a hypophosphite is mixed with mercuric chloride in excess, and a small quantity of hydrochloric acid, and gently heated, care being taken not to let the temperature rise above 60°, as in that case a portion of the mercury may be reduced to the metallic state. The precipitated calomel is washed on a filter, dried at 100°, and weighed. As the atomic weight of calomel is very considerable, and as 4 at. of it correspond to only 1 at. of hypophosphorous acid or of phosphorus (4 × 235·5 or 942 pts. HgCl, to 66 pts. $H^3PO^2$ or 31 pts. P.), the determination may be made with great exactness.

In the solution filtered from the precipitate of calomel, the bases may be determined by the ordinary methods, and the phosphoric acid produced by the oxidation may also be precipitated and estimated, as a verification of the preceding result.

The precipitation of gold from the trichloride by hypophosphorous acid cannot be employed for the estimation of the acid, as the reduction is never complete.

*Hypophosphite of Aluminium.*—A solution of alumina in the cold aqueous acid, evaporated under the air-pump, leaves a thick gum, which gradually dries up to a shining, gummy, brittle mass, not altered by exposure to the air.

*Hypophosphite of Ammonium,* $(NH^4)PH^2O^2$, obtained by precipitating the barium-salt with sulphate of ammonium, evaporating the filtrate to dryness, and exhausting with alcohol, crystallises in large six-sided deliquescent plates, melting at 200° and decomposing at 240°.

*Hypophosphite of Barium.* $Ba''P^2H^4O^4.H^2O$.—Prepared: 1. By warming (not boiling) phosphorus with excess of baryta-water (p. 524), precipitating the excess of baryta with carbonic acid, and evaporating the filtrate to the crystallising-point.—2. Instead of baryta-water, the ordinary yellow solution of barium-sulphide may be used. This when heated with phosphorus, gives off phosphoretted, sulphuretted, and pure hydrogen gases, and forms a solution of hypophosphite and sulphydrate of barium. The latter may be decomposed by carbonate of lead, and the filtered solution, containing only hypophosphite of barium, crystallised by evaporation as before.—3. The salt may also be prepared by dissolving phosphide of barium (i. 507) in water.

Hypophosphite of barium crystallises on cooling from a hot saturated solution, or when its aqueous solution is mixed with alcohol till it begins to show turbidity, usually in nacreous flexible needles containing 1 at. water of crystallisation, which they give off at 100°. They are permanent in the air, soluble in 3 pts. boiling and 3·5 pts. cold water, insoluble in alcohol.

The anhydrous salt, $Ba''P^2H^4O^4$, remains behind when the hydrated salt is heated to 100°, and separates directly from a solution evaporated in vacuo over oil of vitriol; also when the solution mixed with excess of hypophosphorous acid is evaporated by heat. It crystallises in shining square plates unalterable at 100°, but decomposed at a strong heat. The aqueous solution of the salt heated with caustic potash quickly gives off hydrogen and deposits phosphite of barium.

*Hypophosphite of Cadmium* separates from the solution of cadmic carbonate in the cold aqueous acid, by evaporation under the air-pump, in small indistinct crystals.

*Hypophosphite of Calcium.* $Ca''P^2H^4O^4$.—Prepared by boiling phosphorus with excess of lime-water, removing the water as it evaporates, and purified like the barium-salt; also by dissolving phosphide of calcium in water (p. 524). It forms colourless transparent crystals, which, according to H. Rose, are rectangular prisms with two broad, smooth, nacreous faces, while the other faces are glassy and less smooth. According to Wurtz, the salt crystallises in oblique six-sided prisms. It has a bitter taste, is permanent in the air, dissolves in 6 pts. of cold and in a not much smaller quantity of hot water, is insoluble in strong and but slightly soluble in weak alcohol. The crystals do not give off anything at 300°, but decompose at a higher temperature.

*Hypophosphite of Chromium*, $2Cr'''H^3P^2O^4.7H^2O$, or $(Cr^2O^2)''H^2.P^4H^8O^8.5H^2O$, is obtained by decomposing the barium-salt with chromic sulphate and evaporating the filtrate, as a dark-green, amorphous, fissured mass, which gives off water at 200°, and is then insoluble in water and in dilute acids.

*Hypophosphite of Cobalt*, $Co''P^2H^4O^4.6H^2O$, is prepared by dissolving recently precipitated cobaltous hydrate in the aqueous acid, or by decomposing the barium-salt with cobaltous sulphate, and crystallises by evaporation in red efflorescent octahedrons, which give off their 6 at. water of crystallisation at 100°, and are easily soluble in water.

When a solution of hypophosphite of calcium is heated with oxalate of cobalt, no complete decomposition takes place even after a considerable time, and the cobalt-hypophosphite obtained on evaporating the filtrate is said to contain only 3 at. water, and to be less efflorescent than the preceding salt.

*Hypophosphite of Copper*, $Cu''P^2H^4O^4$.—Prepared like the cobalt-salt. The blue solution when very dilute undergoes scarcely any decomposition, even when heated; when somewhat stronger, it decomposes quickly even at 60°, depositing cuprous hydride, CuH (Wurtz). When evaporated in a vacuum, it sometimes yields the salt in blue crystals. (Wurtz.)

*Hypophosphite of Glucinum*.—The solution evaporated in a vacuum over oil of vitriol leaves a thick gum, which dries up to a mass having a vitreous fracture.

*Hypophosphites of Iron*.—The *ferrous salt*, $Fe''P^2H^4O^4.6H^2O$, is formed, with evolution of hydrogen, when metallic iron is dissolved in the aqueous acid. The solution evaporated in a vacuum over oil of vitriol deposits the salt in large green octahedrons, which give off their 6 at. water at 100°. When moist it oxidises very quickly on exposure to the air.

The *ferric salt* is formed by dissolving ferric hydrate in the cold aqueous acid, and separates in the form of a white salt, sparingly soluble in the free acid. Ferric hydrate heated with hypophosphorous acid yields ferric phosphate and ferrous hypophosphite.

*Hypophosphite of Lead*, $Pb''P^2H^4O^4$, is most easily prepared by digesting the aqueous acid with carbonate of lead; if oxide of lead is used, the acid takes up an excess of it, forming an alkaline solution which decomposes when evaporated, depositing phosphate of lead and metallic lead. This decomposition may, however, be prevented by adding a slight excess of acid; and the solution, if then evaporated, deposits the salt in small rhombic prisms often united into plates. It is very slightly soluble in cold, more easily in hot water, forming a slightly acid solution from which it is precipitated by alcohol in nacreous scales. It is permanent at 100°, but decomposes at a stronger heat.

The solution of this salt easily takes up an additional quantity of lead-oxide, acquiring an alkaline reaction; it then decomposes on standing and more quickly if heated, depositing phosphite of lead as a sandy powder. The same decomposition is induced by addition of basic acetate of lead.

The aqueous solution of the neutral salt mixed with a little ammonia deposits a small quantity of lead-hydrate; and the filtrate, which perhaps contains a double salt, yields on boiling a flocculent precipitate of a *basic salt*, said to contain $Pb''P^2H^4O^4.5Pb''O.6H^2O$ or $Pb''P^2H^4O^4.5Pb''H^2O^2.H^2O$. (H. Rose.)

*Hypophosphite of Magnesium*, $Mg''P^2H^4O^4.6H^2O$.—Prepared by double decomposition; crystallises in large, regular, hard, efflorescent octahedrons, easily soluble in water. It gives off 5 at. water at 100°, and the sixth at 180°.

*Hypophosphite of Manganese*, $Mn''P^2H^4O^4.H^2O$, prepared in like manner, crystallises with difficulty in rose-red scalenohedrons, permanent in the air, giving off their water at 100°.

*Hypophosphite of Nickel*, $Ni''P^2H^4O^4.6H^2O$.—Prepared like the cobalt-salt; crystallises in green cubes or octahedrons, which give off their 6 at. water at 100°. When the moist crystals are heated to 120°, or the solution to 100°, partial decomposition takes place, with evolution of hydrogen and precipitation of metallic nickel.

*Hypophosphite of Potassium*, $KPH^2O^2$.—Prepared: 1. By boiling aqueous or alcoholic potash with phosphorus as long as phosphoretted hydrogen continues to escape, then decanting the solution from the undissolved phosphorus, and mixing it

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with acid carbonate of potassium, in order to convert the remaining caustic potash into carbonate. The solution is then evaporated and the residue treated with hot strong alcohol, which dissolves the hyphosphite and leaves the carbonate, the former crystallising out as the solution cools.—2. By decomposing the barium-salt with sulphate of potassium, or the calcium-salt with carbonate of potassium; purified as above by treatment with hot alcohol.

Hypophosphite of potassium usually forms an opaque indistinctly crystalline mass, sometimes however exhibiting six-sided plates. It is very deliquescent, more so than chloride of calcium, easily soluble in water and in weak spirit, less soluble in absolute alcohol, insoluble in ether. It does not lose weight or undergo any alteration at 100°.

*Hypophosphite of Silver.*—Nitrate of silver added to the solution of hypophosphite forms a white precipitate, which however quickly blackens from reduction of the metal.

*Hypophosphite of Sodium*, prepared like the potassium-salt, crystallises in nacreous rectangular tables, somewhat less deliquescent than the potassium-salt, easily soluble in water and in alcohol.

*Hypophosphite of Strontium.* $Sr''P^2H^4O^4$.—Prepared like the barium-salt with hydrate or sulphide of strontium. The solution when evaporated yields the salt in warty crystals, which are easily soluble in water, insoluble in alcohol, permanent in the air, and do not lose weight at 100°.

*Hypophosphite of Zinc.* $Zn''P^2H^4O^4.H^2O$, or with $6H^2O$.—Obtained by dissolving zinc or zinc-oxide in the aqueous acid, or by decomposing the barium-salt with zinc-sulphate. By evaporating the solution it is obtained, sometimes in regular octahedrons containing 6 at. water, very efflorescent, and losing water even when pressed between paper, sometimes in rhombohedral crystals containing 1 at. water, which are permanent in the air. The octahedral salt is mostly formed by spontaneous evaporation of a not too concentrated solution; it gives off its 6 at. water at 100°. The salt is easily soluble in water.

### Phosphorous Oxide, Acid, and Salts.

TRIOXIDE OF PHOSPHORUS, PHOSPHOROUS OXIDE or ANHYDRIDE, $P^2O^3$.—The only reaction which yields this compound is the slow combustion of phosphorus in dry air or oxygen. When phosphorus is exposed at ordinary temperatures to dry air or rarefied oxygen, it glows and becomes coated with trioxide; but the reaction is very imperfect. The ordinary combustion of phosphorus in air produces both phosphorus and phosphoric oxides, together with some suboxide, or perhaps amorphous phosphorus (p. 523). The best mode of preparing the trioxide is to burn phosphorus in a very slow current of perfectly dry air; the trioxide then condenses beyond the phosphorus as a bulky amorphous sublimate.

Phosphorous oxide forms large white flakes readily volatile, and emitting an alliaceous odour. When quite dry it does not redden litmus-paper. It absorbs atmospheric moisture with avidity, and when sprinkled with water dissolves rapidly with a hissing noise, producing phosphorous acid, $P^2O^3 + 3H^2O = 2H^3PO^3$.

PHOSPHOROUS ACID, $H^3PO^3 = \left.\begin{matrix}H\\ P'''\\ H^2\end{matrix}\right\}O^3$.—This acid is produced: 1. By the action of water on the anhydride.—2. By the slow oxidisation of phosphine, this gas when left over well-aërated water being gradually absorbed, with formation of phosphorous acid; again 2 volumes of phosphine unite quietly with 3 volumes of oxygen, when the explosion of the gases is prevented by cooling.—3. By exposing sticks of phosphorus to moist air, phosphoric acid being produced at the same time. (See PHOSPHATIC ACID, p. 499.)

4. By the action of phosphorus on sulphate of copper. When phosphorus is introduced into a solution of this salt (kept saturated by the immersion of crystals), and left to act at the ordinary temperature and with the least possible access of air, copper is first reduced and then converted into black phosphide of copper, and a very acid solution is ultimately obtained, containing nothing but phosphorous and sulphuric acids, the latter of which may be removed by cautious addition of lime or baryta. (Schiff, Ann. Ch. Pharm. cxiv. 200.)

5. By the action of water on trichloride of phosphorus: $3H^2O + PCl^3 = H^3PO^3 + 3HCl$. A current of washed chlorine is slowly passed through a layer of melted phosphorus three or four inches deep, covered by six or eight inches of water, so that each bubble of gas may be completely absorbed by the phosphorus. The trichloride thereby produced is immediately decomposed by contact with the water. The hydrochloric acid produced in the reaction is expelled by evaporation. Great care must be taken to avoid excess of chlorine, as that would give rise to the formation of phosphoric acid.

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6. By the action of trichloride of phosphorus on oxalic acid: 1 at. of the trichloride is poured upon 3 at. crystallised oxalic acid, contained in a retort having its neck directed upwards or provided with a condensing-tube, so that the trichloride which volatilises may flow back again. Violent action immediately takes place, accompanied by evolution of carbonic anhydride, carbonic oxide, and hydrochloric acid; as soon as it is over, the retort is to be gently warmed while a stream of dry carbonic anhydride is passed through it. The mass, which froths at first, gradually settles down into a clear liquid, which solidifies to a radiate mass of phosphorous acid having a slight grey colour. (Hurtzig and Geuther, Ann. Ch. Pharm. cxi. 159.)

*Properties and Reactions.*—Phosphorous acid usually exists in the form of a thick uncrystallisable syrup, but may be obtained in the crystalline state either by the process last described, or by cooling a somewhat concentrated aqueous solution. The crystals, which contain $H^3PO^3$, melt at 74°. The acid in both states is deliquescent. When heated it is resolved into phosphoric acid and phosphine: $4H^3PO^3 = 3H^3PO^4 + PH^3$; hence when heated in the air, it undergoes vivid combustion. According to Hurtzig and Geuther, the crystalline acid, when slowly heated, gives off non-spontaneously inflammable phosphine, producing white fumes.

The aqueous solution of phosphorous acid is a strongly acid liquid which oxidises to phosphoric acid on exposure to the air. It is a powerful reducing agent, decomposing the salts of *silver*, *mercury*, and *gold* in the same manner as hypophosphorous acid; the reduction is much facilitated by saturating the acid with ammonia. When heated with *sulphurous acid*, it yields phosphoric and sulphydric acids:

$$3H^3PO^3 + H^2SO^3 = 3H^3PO^4 + H^2S.$$

If the sulphurous acid is in excess, the sulphydric acid is decomposed and sulphur separated. If the phosphorous acid contains any arsenic, that metal is entirely precipitated as sulphide. *Arsenic acid* is reduced by phosphorous acid to arsenious acid, which, if the materials are dry, is reduced, by fusion with excess of phosphorous acid, to a dark-brown powder of metallic arsenic. Aqueous phosphorous acid dissolves *zinc* and *iron* with evolution of phosphine; it likewise gives off that gas when treated with zinc and sulphuric acid.

**Phosphites.**—Of the three hydrogen-atoms contained in phosphorous acid, only two appear to be replaceable by metals, the acid being in fact dibasic, and forming two series of metallic salts—viz., *neutral phosphites*, $M^2PHO^3$ or $M''PHO^3$, and *acid phosphites*, $MHPHO^3$ or $M''H^2P^2H^2O^6 = M''PHO^3.PH^3O^3$, according to the atomicity of the metal. The third hydrogen-atom of phosphorous acid is more easily replaceable by alcohol-radicles, producing alcoholic phosphorous acids (*e.g.*, ethyl-phosphorous acid, $H^2.PC^2H^5O^3$), still containing two atoms of typic hydrogen, which may be replaced either by metals or by alcohol-radicles. In the latter case phosphites or phosphorous ethers are formed, containing 3 atoms of alcohol-radicle (p. 533), whence the acid has by some chemists been regarded as tribasic; but the view above given accords best with its relations to metallic bases, and with the position which it occupies between monobasic hypophosphorous acid and tribasic phosphoric acid (p. 523). Moreover, in the tri-alcoholic phosphites, $P(C^2H^5)^3O^3$, for example, 2 atoms of the alcohol-radicle may be replaced by metals—for example by $K^2$ or Ba; but the third atom is not thus replaceable (p. 533).

The metallic phosphites are obtained sometimes by acting on the acid with bases, sometimes by double decomposition. They are more stable than the hypophosphites, but are all decomposed by heat. Those which contain water of crystallisation give off hydrogen and leave pyrophosphates: thus—

$$2Ba''PHO^3.H^2O = \overset{\prime\prime}{Ba}{}^2P^2O^7 + 2H^2;$$

but anhydrous neutral phosphites, which do not contain sufficient hydrogen and oxygen for this mode of decomposition, likewise give off phosphoretted hydrogen and leave a more basic phosphate: *e.g.*—

$$5Pb''HPO^3 = Pb''O.2\overset{\prime\prime}{Pb}{}^2P^2O^7 + PH^3 + H^2.$$

The neutral phosphites, excepting those of the alkali-metals, are but sparingly soluble in water, and the lead-salt is almost insoluble; the acid phosphites, however, are soluble. With the chlorides of *barium* and *calcium*, solutions of the alkaline phosphites form white precipitates, soluble in acetic and in phosphorous acid—with *acetate of lead* a white precipitate, insoluble in acetic acid. Solutions of phosphites, unless very concentrated, do not precipitate the solution of a *magnesium-salt* in aqueous ammonia and sal-ammoniac.

The solutions of phosphites undergo but little alteration when exposed to the air at ordinary temperatures, and are not decomposed by boiling with caustic alkalis. They reduce solutions of *gold*, *silver*, and *mercury* in the same manner as the aqueous acid.

The methods to be adopted for the quantitative analysis of phosphites are

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exactly the same as those already described for the hypophosphites (p. 524). Neutral phosphites oxidised by nitric acid, or by hydrochloric acid and chlorate of potassium, are transformed into pyrophosphates:

$$2M^2HPO^3 \quad + \quad O^2 \quad = \quad M^4P^2O^7 \quad + \quad H^2O.$$

Those phosphites which are insoluble or sparingly soluble in water, may be dissolved in hydrochloric acid, and the bases precipitated from them by the usual reagents.

*Phosphite of Aluminium.*—A saturated solution of alum mixed with a strong solution of ammonium-phosphite forms a precipitate which disappears at first, becomes permanent on further addition of ammonia, but does not separate completely till the liquid is boiled. It forms a white powder when dry, and decomposes without incandescence when heated.

*Phosphite of Ammonium*, $(NH^4)^2PHO^3.H^2O$.—Phosphorous acid saturated with ammonia, and evaporated over sulphuric acid in rarefied air, yields this salt in large deliquescent prisms, soluble in 2 pts. of cold and in a smaller quantity of boiling water. In vacuo, at ordinary temperatures, the crystals give off a small quantity of ammonia, and turn acid; at 100° they give off 1 at. water, also with a little ammonia; and at higher temperatures a larger quantity of ammonia, leaving almost pure phosphorous acid, which decomposes when more strongly heated. The aqueous solution when evaporated by heat also gives off ammonia and turns acid.

*Phosphites of Barium.*—The *neutral salt*, $Ba''PHO^3$, is deposited after a few days from a solution of an alkaline phosphite mixed with chloride of barium, as a crystalline crust containing ½ at. water ($2Ba''PHO^3.H^2O$). It is but sparingly soluble in cold water, and is decomposed by boiling with water into an insoluble basic and a soluble acid salt. It is slightly efflorescent, and gives off its water of crystallisation between 150° and 200°.

The *acid salt*, $Ba''H^2P^2H^2O^6.H^2O$, is obtained by digesting the neutral salt with a quantity of phosphorous acid not quite sufficient to dissolve it, or by adding baryta or carbonate of barium to phosphorous acid as long as it continues to dissolve, and evaporating the filtrate to a syrup at a gentle heat. On leaving this liquid in vacuo over oil of vitriol, the acid salt is deposited in warty crystals. It is soluble in water but insoluble in alcohol. The aqueous solution decomposes when boiled, the neutral salt separating, and a more acid salt, not yet examined, remaining in solution. The salt gives off 1 at. water at 100°.

*Phosphite of Bismuth*, obtained by double decomposition, is a white precipitate which when ignited after drying gives off pure hydrogen.

*Phosphite of Cadmium.*—White precipitate, which gives off hydrogen when distilled, and leaves a residue containing a small quantity of metallic cadmium.

*Phosphites of Calcium.*—The *neutral salt*, $Ca''PHO^3.H^2O$, separates after a while from a solution of the ammonium-salt mixed with chloride of calcium, as a crystalline crust sparingly soluble in cold water. The solution decomposes when heated, depositing a basic salt (? tricalcic phosphite, $\overset{''}{Ca}{}^3P^2O^6$), while an acid salt remains dissolved. The neutral salt gives off its water at 100°.

The *acid salt*, $Ca''H^2P^2H^2O^6.H^2O$, is obtained, by acting upon marble with aqueous phosphorous acid, as long as carbonic anhydride continues to escape, as a crystalline crust made up of needle-shaped crystals. It is soluble in water, and the solution mixed with alcohol deposits the neutral salt, while a very acid salt remains dissolved. The crystals give off their water at 100°.

*Phosphite of Chromium* is precipitated on mixing chromic chloride with an alkaline phosphite, but does not separate completely till the liquid is heated. When dry it is a loose grey powder, which is decomposed by heat, with evolution of pure hydrogen.

*Phosphite of Cobalt* is also obtained by precipitation, and separates completely only when the liquid is heated. In the dry state it is a pale-red powder, which when heated first turns violet, then black, and afterwards decomposes with incandescence and evolution of hydrogen.

*Phosphite of Copper*, $Cu''PHO^3.2H^2O$.—Obtained in the pure state, as a blue granulo-crystalline precipitate, on mixing a solution of cupric acetate with aqueous phosphorous acid; less pure, as a bluish-white flocculent precipitate, by treating cupric sulphate with an alkaline phosphite. It gives off water when gently heated, and at a higher temperature evolves hydrogen, and leaves cupric phosphate mixed with metallic copper. A solution of cupric phosphite in aqueous phosphorous acid also decomposes when heated, with separation of metallic copper.

*Phosphite of Glucinum* is a gummy precipitate, white and pulverulent when dry, insoluble in water, decomposing when heated, with incandescence and evolution of pure hydrogen.

*Phosphites of Iron.*—The *ferrous salt* is a white precipitate, which in the moist state oxidises quickly in the air, turning first green and then brown. When heated it gives off pure hydrogen.

*Ferric salt.*—Neutral ferric salts are completely precipitated by alkaline phosphites only after long standing or with the aid of heat. The dried precipitate is white and pulverulent; it glows when heated, giving off hydrogen mixed with a little phosphoretted hydrogen.

*Phosphites of Lead.*—The *neutral salt*, $Pb''PHO^3$, is obtained by precipitating neutral acetate of lead with phosphorous acid or phosphite of ammonium. It is a white precipitate nearly insoluble in water, and dissolving but sparingly in aqueous phosphorous acid, much more easily in nitric acid, which does not oxidise it in the cold; it is easily oxidised, however, when heated with nitric or sulphuric acid. It does not give off any water at 100°, but decomposes at higher temperatures, with evolution of hydrogen and phosphoretted hydrogen, and leaves a phosphate of lead (p. 528) mixed with a little phosphide.

A compound of this salt with chloride of lead is precipitated on mixing a boiling solution of chloride of lead with pure phosphite of ammonium, or with trichloride of phosphorus which has been decomposed by water and then neutralised with ammonia. By continued washing with boiling water however, this double salt is decomposed, the whole of the chloride of lead being removed, and pure phosphite remaining behind.

A *basic phosphite of lead*, $2(Pb''O.Pb''PHO^3).H^2O$, is formed on digesting the recently precipitated neutral salt with ammonia in a flask, and afterwards washing it with alcohol (H. Rose). Another basic salt, $Pb''O.2Pb''PHO^3$, is formed by precipitating basic acetate of lead with phosphite of ammonium.

*Phosphite of Magnesium* is obtained by digesting the aqueous acid with basic carbonate of magnesium, and evaporating the filtrate under an exhausted receiver, as a crystalline crust sparingly soluble in water. When heated it gives off water of crystallisation, and at a higher temperature decomposes with vivid incandescence.

Phosphite of magnesium forms a sparingly soluble double salt with phosphite of ammonium—much more soluble, however, than the corresponding phosphate.

*Phosphite of Manganese*, $2Mn''PHO^3.H^2O$, obtained by adding an alkaline phosphite to the solution of a manganous salt till none of the latter remains in excess, is a reddish-white precipitate which is not quite insoluble in water, gives off its water of crystallisation in drying, and decomposes at a stronger heat, with vivid incandescence, and evolution of hydrogen and phosphoretted hydrogen.

*Phosphites of Potassium.*—The *neutral salt*, $K^2HPO^3$, is obtained by saturating the aqueous acid with potash, and evaporating under the air-pump, as a syrupy mass in which crystals form after some time only. It is deliquescent, easily soluble in water, insoluble in alcohol.

An *acid phosphite of potassium*, $K^2H^7P^3O^9 = K^2PHO^3.2PH^3O^3$, is produced by exactly neutralising 1 pt. of aqueous phosphorous acid with hydrate or carbonate of potassium, then adding 2 pts. of the same acid, and evaporating in vacuo. The liquid then solidifies completely to a mass of laminar crystals, unctuous to the touch, having a strongly acid taste, and very soluble in water. The salt does not lose weight at 200°, but decomposes at 250°, with evolution of hydrogen and phosphoretted hydrogen.

An acid potassium-salt analogous to the other acid phosphites has not yet been obtained. A solution of the neutral salt mixed with as much phosphorous acid as it already contains, and evaporated in a vacuum, yields after some time a crystalline crust of the acid salt just described, the syrupy mother-liquor retaining nothing but neutral salt.

*Phosphites of Sodium.*—The *neutral salt*, $Na^2PHO^3.5H^2O$, is obtained by neutralising the aqueous acid with soda and evaporating in a vacuum, as a thick syrup, which after some time solidifies to a crystalline mass. According to Dulong, the individual crystals are rhombohedrons, approaching very nearly to cubes. They are easily soluble in water and in alcohol, hygroscopic, and deliquesce quickly on exposure to the air, but effloresce in vacuo over oil of vitriol, and give off all their water of crystallisation at 100°.

The *acid salt*, $2Na^2H^7P^3O^9.H^2O$, is analogous in composition to the acid potassium-salt (excepting that it contains water of crystallisation), and is obtained in a similar manner. The solution crystallises completely by evaporation in vacuo, yielding shining prisms very soluble in water, permanent in dry air, but quickly deliquescing in air of the ordinary degree of humidity. The salt gives off its water of crystallisation at 200°, and decomposes at 250°, evolving a large quantity of phosphoretted hydrogen.

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*Phosphite of Strontium*, $2Sr''PHO^3.H^2O$, is prepared by saturating phosphorous acid with carbonate of strontium and evaporating. A solution of chloride of strontium mixed with phosphite of ammonium yields a scanty precipitate, which increases on evaporating the liquid. Phosphite of strontium is sparingly soluble in water, and is decomposed by boiling with water into a soluble acid salt and an insoluble nacreous basic salt. The dry salt is decomposed by heat, with evolution of hydrogen.

*Phosphites of Tin.*—The *stannous salt*, $Sn''PHO^3$, is prepared by precipitating stannous chloride with aqueous phosphorous acid, and thoroughly washing the precipitate with water. It is white, insoluble in water, but soluble in hydrochloric acid, forming a solution which is an extremely powerful reducing agent. The dry salt decomposes with intumescence when heated, giving off phosphoretted hydrogen, and leaving a black residue.

The *stannic salt* is obtained by mixing aqueous stannic chloride with an alkaline phosphite, as a white precipitate which dries up to a vitreous brittle mass. When strongly heated it gives off, not hydrogen but water, leaving a stannous salt soluble in hydrochloric acid.

*Phosphite of Titanium.*—A solution of titanic chloride yields with phosphite of ammonium a white precipitate, which when ignited gives off hydrogen and phosphoretted hydrogen, and leaves a black residue containing phosphoric and titanic oxides.

*Phosphite of Zinc*, $2Zn''PHO^3.5H^2O$.—Alkaline phosphites precipitate sulphate of zinc imperfectly in the cold, completely when heated. The white precipitate is sparingly soluble in water, gives off its water in drying, and when more strongly heated gives off hydrogen, mixed towards the end with phosphoretted hydrogen.

**Alcoholic Phosphites. Phosphorous Ethers.** Phosphorous acid, though dibasic acid, is capable, as already observed, of forming ethers in which 1, 2, or 3 atoms of hydrogen are replaced by alcohol-radicles. If one of the three hydrogen-atoms be regarded as alcoholic (ii. 915), and the other two as basylous, these ethers may be represented by the following formulæ, in which R denotes a monatomic alcohol radicle:

$$\text{Mono-alcoholic phosphorous ethers}\quad H^2.PRO^3 = \left.\begin{matrix}R\\P'''\\H^2\end{matrix}\right\}O^3$$

$$\text{Di-alcoholic phosphorous ethers}\quad RH.PRO^3 = \left.\begin{matrix}R\\P'''\\HR\end{matrix}\right\}O^3$$

$$\text{Tri-alcoholic phosphorous ethers}\quad R^2.PRO^3 = \left.\begin{matrix}R\\P'''\\R^2\end{matrix}\right\}O^3$$

Those which contain 1 or 2 atoms of alcohol-radicle are acid ethers capable of forming metallic salts; those which contain 3 atoms of alcohol-radicle are neutral. The acid ethers are produced by the action of trichloride of phosphorus on the corresponding hydrated alcohols; the neutral ethers by the action of trichloride of phosphorus on the corresponding sodium-alcohols.

There might also be mono- and di-alcoholic phosphites, constituted according to the formulæ $HR.PHO^3$ and $R^2.PHO^3$.

AMYLIC PHOSPHITES.—*Amylphosphorous acid*, $C^5H^{13}PO^3 = H^2.PC^5H^{11}O^3$. (Wurtz, Ann. Ch. Phys. [3] xvi. 227; Ann. Ch. Pharm. lviii. 75.)—This and the following compound are produced by the action of trichloride of phosphorus on amylic alcohol. One vol. trichloride of phosphorus is slowly dropped into 1 vol. amylic alcohol, and a small quantity of water very slowly added, the vessel being well cooled. After all the excess of chloride of phosphorus has been decomposed by the water, the mixture is shaken up with an equal volume of water; the oily mixture of amylphosphorous acid and amylic amylphosphite, which rises to the surface on leaving the liquid at rest, is decanted and freed from hydrochloric acid by repeated washing with water; and the amyl phosphorous acid is extracted by a weak solution of sodic carbonate (a strong solution would likewise dissolve the amylic amylphosphite). The alkaline solution is then separated mechanically from the amylic amylphosphite which floats on the surface; the portion which still remains dissolved therein is separated by agitation with common ether; and the alkaline solution is supersaturated with hydrochloric acid, whereby the amylphosphorous acid is separated, with strong turbidity, and at first rises to the surface in the form of an oil, in consequence of containing ether, but sinks to the bottom after the ether is evaporated. Lastly, to free this oil from chloride of sodium, it is dissolved in water, reprecipitated by hydrochloric acid, gently heated after the hydrochloric acid has been decanted, and placed in a vacuum, to remove the water and hydrochloric acid.

Amylphosphorous acid is an oil which sinks in water; it is nearly inodorous in the fresh state, but strongly acid; dissolves readily in *water*, and is precipitated therefrom by hydrochloric acid. It yields by dry distillation a large quantity of combustible gas, and a small quantity of liquid distillate, leaving phosphorous acid, which when more strongly heated, gives off phosphoretted hydrogen gas. It burns with a very smoky flame, leaving phosphorous acid. It reduces *silver-salts.* After being kept for some time it no longer dissolves completely in water, and the solution quickly decomposes into amylic alcohol and phosphorous acid. The acid, separated by hydrochloric acid from the sodium-salt which has been kept for some time, likewise exhibits this behaviour. This change of properties is perhaps due to the conversion of the amylphosphorous acid, $\mathrm{H^2.PC^5H^{11}O^3}$, into *monamylicphosphite*, $\mathrm{C^5H^{11}.H.PHO^3}$.

Amylphosphorous acid decomposes alkaline carbonates with effervescence; its salts decompose readily. The *potassium-* and *sodium-salts* can only be obtained in the gelatinous state. The *barium-salt* dries up in vacuo to a soft deliquescent mass. The *lead-salt* is a white curdy precipitate, which decomposes even in the dry state, and quickly when moist, giving off an odour of fusel-oil.

β. *Monamylic Amylphosphite*, $\mathrm{C^{10}H^{23}PO^3 = H.C^5H^{11}.PC^5H^{11}O^3}$. (Wurtz, *loc. cit.*)—Obtained as above, and freed from amylphosphorous acid by washing with dilute sodic carbonate till the residue no longer reddens litmus; it is then washed with water, and heated several times in vacuo to 80°—100° to drive off water and amylic chloride. Should the product be coloured, in consequence of the temperature during the reaction having been allowed to rise too high, it must be rectified in vacuo; but this process is always attended with a certain amount of decomposition.

Amylic amylphosphite is a colourless or pale-yellow oil, of specific gravity 0·967 at 19°. It boils only at a high temperature, and with some decomposition; smells slightly of amylic alcohol, and has a very pungent disagreeable taste.

When passed in the state of vapour through a red-hot tube, it yields gases, among which phosphoretted hydrogen occurs. It may be set on fire by a flaming body when strongly heated; paper soaked in it burns when set on fire, with a white phosphorus flame. It absorbs *chlorine gas*, with rise of temperature and evolution of hydrochloric acid; in the dark at 0° there is formed hereby a product containing 1 at. chlorine; but under the influence of heat and light, products very rich in chlorine are formed; these bodies are colourless and viscid, and decompose after a while, with evolution of hydrochloric acid. *Nitric acid* acts violently on amylic amylphosphite, yellow oily drops passing over, and a strong odour of valerianic acid being evolved. When it is boiled with solution of *nitrate of silver*, there is formed, with a certain amount of reduction, a black magma containing phosphate of silver. When exposed to moist air or kept in loosely closed vessels, it gradually turns acid. By boiling aqueous *alkalis*, it is quickly resolved into amylic alcohol, which passes over, and a residue of alkaline phosphite.

*Diamylic Amylphosphite*, $\mathrm{C^{15}H^{33}PO^3 = (C^5H^{11})^2PC^5H^{11}O^3}$. (Railton, Chem. Soc. Qu. J. vii. 218.)—Produced by the action of trichloride of phosphorus on amylate of sodium, the preparation being conducted in the same manner as for the corresponding ethyl-compound (p. 533):

$$\mathrm{3C^5H^{11}NaO + PCl^3 = C^{15}H^{33}PO^3 + 3NaCl.}$$

It is an oily neutral liquid, having a very offensive odour, and decomposing more easily than diethylic ethylphosphite. It boils in hydrogen at 236°, is insoluble in water, soluble in alcohol and in ether.

ETHYLIC PHOSPHITES.—*Ethylphosphorous acid*, $\mathrm{C^2H^7PO^3}$ =

$$\mathrm{H^2.PC^2H^5O^3} = \left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{P'''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^3}.$$

(Wurtz, Ann. Ch. Phys. [3] xvi. 218.)—Produced by the action of trichloride of phosphorus on hydrated alcohol:

$$2\left[\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right] + \mathrm{H^2O} + \mathrm{PCl^3} = \left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{P'''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^3} + \mathrm{C^2H^5Cl} + \mathrm{2HCl.}$$

Trichloride of phosphorus is added drop by drop to the alcohol, in a vessel kept continually cold from without; and the mixture is evaporated at a gentle heat, to drive off the chloride of ethyl and hydrochloric acid, first in the air, and afterwards in vacuo, the vessel containing the liquid being connected with an air-pump by a tube containing hydrate of potassium. The remaining syrup is then saturated with carbonate of barium, and separated by filtration from phosphite of barium; the filtrate is evaporated in vacuo; the dry residue treated with absolute alcohol; the liquid filtered to separate the chloride of barium, and evaporated till the barium-salt crystallises.

The acid itself is scarcely known, in consequence of its great tendency to resolve itself into phosphorous acid and alcohol.

It is capable of exchanging one or both of its basylous hydrogen-atoms either for metals or for alcohol-radicles, thereby forming both acid and neutral salts. The acid metallic salts are produced by treating the acid with the respective bases (Wurtz), the neutral salts by the action of strong bases on the neutral ethylic ether or diethylic ethylphosphite.

*Barium-salts.*—The *acid salt*, $Ba''H^2.P^2(C^2H^5)^2O^6$, obtained as above in the preparation of the acid, is a white, amorphous, friable, deliquescent mass, which swells up when subjected to dry distillation, giving off, first certain volatile products of the decomposition of alcohol, then phosphoretted hydrogen-gas, and leaving a mixture of barytic phosphate and oxide of phosphorus (or red phosphorus). It is permanent when dry, but in solution it is gradually resolved into alcohol and barytic metaphosphate, which crystallises out:

$$Ba''H^2.P^2(C^2H^5)^2O^6 \quad + \quad O^2 \quad = \quad 2(C^2H^5.H.O) \quad + \quad Ba''P^2O^6.$$

It is very soluble in water and alcohol, and is precipitated from the alcoholic solution by ether. (Wurtz.)

The *neutral barium-salt*, $Ba''PC^2H^5O^3$, is produced by adding 1 at. diethylic ethylphosphite to 1 at. hydrate of barium dissolved in hot water:

$$(C^2H^5)^2PC^2H^5O^3 \quad + \quad Ba''H^2O^2 \quad = \quad Ba''PC^2H^5O^3 \quad + \quad 2(C^2H^5.H.O).$$

On gently heating the mixture, alcohol is given off, and the remaining liquid deposits the barium-salt on evaporation. It does not crystallise. It may be evaporated in a water-bath without decomposing, but on boiling it is easily resolved into *alcohol* and monobarytic phosphite (p. 529).

$$2Ba''PC^2H^5O^3 \quad + \quad 3H^2O \quad = \quad 2(C^2H^5.H.O) \quad + \quad 2Ba''PHO^3.H^2O.$$

By decomposing this salt with various sulphates, other neutral ethylphosphites may be obtained, but none of them crystallise. (Railton, Chem. Soc. Qu. J. vii. 219.)

The *acid copper-salt*, obtained by precipitating the acid barium-salt with sulphate of copper, and evaporating the filtrate in vacuo, is a blue, amorphous, soft, deliquescent mass, in which the copper is gradually reduced. (Wurtz.)

The *acid lead-salt*, obtained by saturating the acid with recently precipitated carbonate of lead, and evaporating the filtrate in vacuo, forms shining, unctuous, crystalline scales, permanent in the air, soluble in water and alcohol, insoluble in ether. The aqueous solution gradually deposits phosphite of lead. (Wurtz.)

The *acid potassium-salt*, obtained by precipitating the barium-salt with sulphate of potassium, and evaporating in vacuo, is a thick uncrystallisable syrup. (Wurtz.)

*Ethylobarytic Ethylphosphite*, $C^8H^{20}Ba''P^2O^6 = (C^2H^5)^2Ba''(PC^2H^5O^3)^2 = \left.\begin{matrix}(C^2H^5)^2\\(P''')^2\\Ba''(C^2H^5)^2\end{matrix}\right\}O^6$.—This salt is obtained by adding 2 at. diethylic ethylphosphite to 1 at. hydrate of barium dissolved in hot water, and gently heating the liquid for a few minutes. Alcohol is then given off, and the liquid, if carefully evaporated on a water-bath, deposits the salt as a confused crystalline mass:

$$2\left[\left.\begin{matrix}C^2H^5\\P'''\\(C^2H^5)^2\end{matrix}\right\}O^3\right] \quad + \quad Ba''H^2O^2 \quad = \quad \left.\begin{matrix}(C^2H^5)^2\\(P''')^2\\(C^2H^5)^2Ba''\end{matrix}\right\}O^6 \quad + \quad 2(C^2H^5H.O).$$

This salt is very deliquescent, extremely soluble in water, soluble also in dilute alcohol, but only slightly soluble in absolute alcohol. It does not decompose at 108°. (Railton.)

*Ethylopotassic Ethylphosphite*, $C^2H^5.K.PC^2H^5O^3$, is obtained by decomposing the barium-salt with potassic sulphate. It crystallises with difficulty in thin plates radiating from a centre. It is deliquescent, soluble in alcohol, insoluble in ether.

The *sodium-salt* prepared in like manner resembles the potassium-salt, but has not been obtained in the crystalline state. The *nickel-*, *iron-*, *zinc-*, and *magnesium*-salts obtained in like manner are also non-crystalline, and extremely soluble in water, but appear to be insoluble in alcohol. On decomposing the solution of the barium-salt with cupric sulphate, the copper was reduced, even in a vacuum. (Railton.)

The corresponding *hydrogen-salt*, or *ethylic ethylphosphite*, $H.C^2H^5.PC^2H^5O^3$, has not yet been obtained.

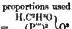
*Diethylic Ethylphosphite*, $C^6H^{15}PO^3 = \left.\begin{matrix}C^2H^5\\P'''\\(C^2H^5)^2\end{matrix}\right\}O^3$. (Railton, Chem. Soc. Qu. J. vii. 216.)—Produced by the action of trichloride of phosphorus on ethylate of sodium:

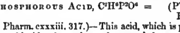
$$3C^2H^5NaO \quad + \quad PCl^3 \quad = \quad C^6H^{15}PO^3 \quad + \quad 3NaCl.$$

1 at. trichloride of phosphorus mixed with five times its bulk of pure ether is added by small portions to 3 at. ethylate of sodium (prepared by acting on perfectly anhydrous

alcohol with sodium in a retort provided with a condensing-tube, and evaporating to dryness at 120°), the retort being kept at the boiling-point of ether by a water-bath. The ether is then distilled off, and the retort transferred to an oil-bath, in which it is gradually heated to 200°, and kept at that temperature till the whole of the ethylic phosphite has distilled over. The distillate is rectified several times in a current of hydrogen, the portion which comes over at 188° being each time collected.

Diethylic ethylphosphite is a neutral somewhat oily liquid, having a peculiarly offensive odour. Specific gravity = 1·075 at 15·5°. Boiling-point in air, 191°; in hydrogen, 188°. Vapour-density, taken in an atmosphere of hydrogen, = 5·800 and 5·877; calc. (2 vol.) = 5·763. It is soluble in water, alcohol, and ether, and burns with a bluish-white flame. Heated with baryta-water, it yields the barium-salt (or ethyl-barium-salt) of ethylphosphorous acid, according to the proportions used (p. 533).

**ACETYL-PYROPHOSPHOROUS ACID**, $C^2H^6P^2O^6$ =  $\left.\begin{array}{c}H.C^2H^3O\\(P''')^2\\H^2\end{array}\right\}O^5$. (N. Menschutkin, Ann. Ch. Pharm. cxxxiii. 317.)—This acid, which is produced by the action of phosphorous acid on chloride of acetyl, may be regarded as resulting from the substitution of acetyl for hydrogen in a hypothetical pyrophosphorous acid, $P^2H^4O^5$, related to phosphorous acid in the same manner as pyrophosphoric to orthophosphoric acid:



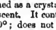
$$2\left[\left.\begin{array}{c}P'''\\H^3\end{array}\right\}O^3\right] \quad - \quad H^2O \quad = \quad \left.\begin{array}{c}P^2\\H^4\end{array}\right\}O^5.$$

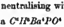
Phosphorous acid. Pyrophosphorous acid.

To prepare it, 1 at. phosphorous acid and 1 at. chloride of acetyl are heated together in a sealed tube to 120°, in an oil-bath for 50 to 55 hours, the tube being opened two or three times during the process to give vent to the large quantity of hydrochloric acid which is set free. When the reaction is complete, the whole of the chloride of acetyl is found to have disappeared, and the tube contains a perfectly white crystalline mass, consisting of acetyl-pyrophosphorous acid:

$$2PH^3O^3 \quad + \quad 2C^2H^3OCl \quad = \quad H^3P(C^2H^3O)O^5 \quad + \quad C^2H^4O^2 \quad + \quad 2HCl.$$

To purify this product, it is first dried in a stream of carbonic anhydride, whereupon hydrochloric and acetic acids pass off; then converted into a potassium-salt, which is purified by two or three crystallisations; from this the lead-salt is prepared by precipitation; and the precipitate decomposed by sulphydric acid yields a solution of pure acetyl-pyrophosphorous acid. On evaporating this solution to a syrup, and leaving it over oil of vitriol, the acid is obtained as a crystalline mass, very much like crystallised phosphorous acid, but less deliquescent. It contains $P^2(C^2H^3O)H^3O^5.2H^2O$; gives off its water of crystallisation at 100°; does not fuse, but decomposes when strongly heated, giving off phosphoretted hydrogen.

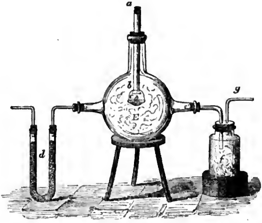
Acetyl-pyrophosphorous acid appears to be dibasic, forming salts which may be represented by the general formula,  $\left.\begin{array}{c}H.C^2H^3O\\(P''')^2\\M^2\end{array}\right\}O^5$. The *potassium-salt* forms crystals, which contain $P^2(C^2H^3O)HK^2O^5.2\frac{1}{2}H^2O$, give off $1\frac{1}{2}H^2O$ at 100°, and the remaining 1 at. at 120°. The crystals are very soluble in water, and effloresce quickly, splitting at the same time into lumps, in an easily-determined direction of cleavage. By boiling with excess of potash, the salt is resolved into acetate and phosphite of potassium.—The *barium-salt*, $P^2(C^2H^3O)HBa''O^5$, obtained from the potassium-salt by double decomposition, is a precipitate which becomes crystalline after a while.—The *lead-salt*, $P^2(C^2H^3O)HPb''O^5$, is a white precipitate.—*Nitrate of silver* forms with the potassium-salt a white precipitate, from which when thrown on a filter the silver is instantly reduced.

**TRITYLENE-PHOSPHOROUS ACID**, $C^3H^7PO^3$ =  $\left.\begin{array}{c}(C^3H^6)'\\P'''\\H\end{array}\right\}O^3$?—Kane, by acting on acetone with iodine in presence of phosphorus, and neutralising with carbonate of barium, obtained a salt to which he assigned the formula $C^6H^5Ba^4PO^4$ or $C^3H^6Ba^2PO^2$. According to E. Mulder, however (J. pr. Chem. xci. 472), if the product of the reaction be freed from iodine by digestion with water and agitation with mercury, then neutralised with carbonate of barium, and the resulting barium-salt purified by repeated precipitation with alcohol from the aqueous solution, it finally exhibits the composition of *tritylene-phosphite of barium*, $(C^3H^6)^2Ba''P^2O^6$ (Mulder regards it as a phosphite of barium and acetone). The solution of this salt treated with carbonate of sodium, yields a precipitate of barytic carbonate and a solution of *tritylene-phosphite of sodium*, $(C^3H^6)''NaPO^3$, which remains on evaporation as an amorphous mass.

### Phosphoric Anhydride, Acids, and Salts.

Pentoxide of Phosphorus, Phosphoric Oxide or Anhydride, $P^2O^5$. —This oxide is the sole product of the rapid combustion of phosphorus in excess of dry air or oxygen. The combustion is easily effected in a large three-necked glass globe E (*fig.* 737), in the centre of which is suspended a porcelain dish *c*, attached by means of platinum-wire to the wide tube *a b*, which is closed at *a* with a cork. One of the lateral openings of the globe communicates with a U-tube *d*, containing pumice soaked in oil of vitriol to dry the air which enters the globe, while the other lateral opening communicates with a wide-mouthed bottle *f*, destined to receive the product. The phosphorus in the capsule is ignited by a hot wire, the cork inserted in the vertical tube, and a current of dry air passed through the apparatus by means of an aspirator connected with the exit-tube *g* of the bottle *f*, or by a blower attached to the drying-tube *d*, or by other means. From time to time fresh pieces of phosphorus are dropped into the capsule through the vertical tube, which is recorked after each addition. The phosphoric oxide produced by the combustion condenses as a white deposit in the globe and in the bottle *f*. If the supply of air is not sufficient, the product will be contaminated with phosphorous oxide.

*Fig.* 737.



A simplified apparatus for preparing phosphoric anhydride is described by Grabowski (Ann. Ch. Pharm. cxxxvi. 119).

Phosphoric oxide, as above prepared, forms a snow-white, flocculent, amorphous deposit, inodorous when free from phosphorous oxide, and not affecting litmus-paper when perfectly dry. It sublimes below a red heat. When heated with charcoal it is decomposed, yielding carbonic oxide and phosphorus. It is also decomposed when heated with easily oxidisable metals. Heated with pentachloride of phosphorus (Weber, p. 513), or with perfectly dry chloride of sodium (Lautemann, Ann. Ch. Pharm. cxiii. 240), it yields phosphoric oxychloride $POCl^3$. It has a powerful attraction for water, dissolving in it with a hissing noise and great development of heat, and deliquescing quickly in contact with moist air. It likewise acts as a powerful dehydrating agent, abstracting water from acids, alcohols, and many other bodies when heated with them. Strong sulphuric acid, for example, heated with phosphoric anhydride is converted into sulphuric anhydride. It unites with water in three proportions, forming three acids, $H^2O.P^2O^5$, $2H^2O.P^2O^5$, and $3H^2O.P^2O^5$, denoted by the generic name of phosphoric acids. At a red heat it expels the volatile anhydrides from their salts, producing phosphates containing various proportions of base, according to the facility with which the volatile anhydride is expelled. (Odling, Phil. Mag. [4] xviii. 168; Jahresb. 1859, p. 151.)

Phosphoric acid.—Phosphoretted hydrogen, $PH^3$, burnt in air or oxygen takes up 4 atoms of oxygen and forms phosphoric acid, $H^3PO^4$. The same acid is also produced by the oxidation of hypophosphorous or phosphorous acid; by oxidising phosphorus with nitric acid; by the decomposition of apatite and other native phosphates; and by the action of boiling water on phosphoric anhydride. This acid is tribasic, forming three distinct classes of metallic salts. With sodium, for example, it forms the three salts $NaH^2PO^4$, $Na^2HPO^4$, and $Na^3PO^4$, the first two of which, still containing replaceable hydrogen, are acid salts, while the third is neutral. The three atoms of hydrogen in phosphoric acid may be replaced in like manner by alcohol-radicles, forming acid and neutral ethers.

If now monosodic phosphate, $NaH^2PO^4$, be heated to redness, it gives off 1 atom of water and leaves an anhydrous monosodic phosphate, $NaPO^3 = NaH^2PO^4 - H^2O$, the aqueous solution of which, when treated with nitrate of lead, yields a lead-salt of corresponding composition: thus—

$$2NaPO^3 + Pb''(NO^3)^2 = Pb''(NO^3)^2 + 2NaNO^3;$$

and this lead-salt, decomposed by sulphydric acid, yields a monohydric acid having the composition $HPO^3$, possessing properties quite distinct from those of the trihydric acid above mentioned:

$$Pb''(PO^3)^2 + H^2S = 2HPO^3 + Pb''S.$$

The trihydric acid which is produced by the oxidation of phosphorus, and by the decomposition of the ordinary native phosphates, is called **orthophosphoric acid** or **ordinary phosphoric acid**; the monohydric acid is called **metaphosphoric acid**. The former may be regarded as a trihydrate, the latter as a monohydrate of phosphoric anhydride:

$$2H^3PO^4 = 3H^2O.P^2O^5 \text{ orthophosphoric acid.}$$
$$2HPO^3 = H^2O.P^2O^5 \text{ metaphosphoric acid.}$$

Both are soluble in water, and the former may be produced by the action of boiling water, the latter of cold water on phosphoric anhydride. They are easily distinguished from one another by their reactions with albumin and with nitrate of silver. Metaphosphoric acid coagulates albumin, and gives a white precipitate with nitrate of silver; whereas orthophosphoric acid does not coagulate albumin, and gives no precipitate, or a very slight one, with nitrate of silver, till it is neutralised with an alkali, in which case a yellow precipitate is formed.

Metaphosphoric acid and its salts differ from orthophosphoric acid and the orthophosphates by the want of one or two atoms of water or base, the relation between the two classes of salts being similar to that between ortho- and meta-silicates, carbonates, &c. (p. 238): thus—

| Metaphosphates. | | Orthophosphates. | | |
|---|---|---|---|---|
| $HPO^3$ | = | $H^3PO^4$ | − | $H^2O$ |
| $NaPO^3$ | = | $NaH^2PO^4$ | − | $H^2O$ |
| $Ba''P^2O^6$ | = | $Ba''H^4P^2O^8$ | − | $2H^2O$ |
| $AgPO^3$ | = | $Ag^3PO^4$ | − | $Ag^2O$ |
| $Pb''P^2O^6$ | = | $Pb^3P^2O^8$ | − | $2Pb''O$ |

Accordingly, we find that metaphosphates and orthophosphates are convertible one into the other by the loss or gain of one or two atoms of water or base: thus—

*α*. A solution of metaphosphoric acid is converted, slowly at ordinary temperatures, quickly at the boiling heat, into orthophosphoric acid, and the metaphosphates of sodium and barium are converted by boiling with water into the corresponding monometallic orthophosphates (see the first three equations above).—*β*. The metaphosphate of a heavy metal, silver or lead for example, is converted by boiling with water into trimetallic phosphate and orthophosphoric acid:

$$3AgPO^3 + 3H^2O = Ag^3PO^4 + 2H^3PO^4.$$

*γ*. When any metaphosphate is fused with an oxide, hydrate or carbonate, it becomes a trimetallic orthophosphate: *e.g.*—

$$NaPO^3 + Na^2CO^3 = Na^3PO^4 + CO^2.$$

On the other hand: (*δ*), when orthophosphoric acid is heated to redness, it loses water and becomes metaphosphoric acid; and when a monometallic orthophosphate is heated to redness, it also loses water and is transformed into a metaphosphate. Or if one of the bases of a dimetallic orthophosphate is volatile, a metaphosphate is likewise produced by heating the salt to redness; thus with sodio-ammonic orthophosphate (microscosmic salt):

$$Na(NH^4)HPO^4 - (NH^4)HO = NaPO^3.$$

*ε*. A trimetallic orthophosphate fused with a fixed anhydride, silicic or boric, for example, is converted into a metaphosphate by abstraction of an atom of base: thus—

$$Na^3PO^4 + SiO^2 = Na^2SiO^3 + NaPO^3.$$

When phosphoric anhydride is fused with the salt of a volatile anhydride, an ortho- or meta-phosphate is produced, according to the facility with which the volatile anhydride can be expelled from the base. Thus with sulphate of magnesium, the product is an orthophosphate:

$$P^2O^5 + 3Mg''SO^4 = \overset{''}{Mg}{}^3P^2O^8 + 3SO^3;$$

but with sulphate of potassium, in which the sulphuric anhydride is retained with greater force, a metaphosphate is produced, thus:—

$$P^2O^5 + K^2SO^4 = 2KPO^3 + SO^3.$$

Intermediate between ortho- and meta-phosphates there are at least three distinct classes of salts, the most important which are the **pyrophosphates** or **paraphosphates**, $M^4P^2O^7$ or $\overset{''}{M}{}^4P^4O^{14}$. These salts may be viewed as compounds of 1 at. orthophosphate and 1 at. metaphosphate: $M^4P^2O^7 = M^3PO^4 + MPO^3$.

Pyrophosphate of sodium is produced by heating disodic orthophosphate to redness, thus:—

$$2Na^2HPO^4 = Na^4P^2O^7 + H^2O.$$

The solution of this salt yields insoluble pyrophosphates with lead and silver salts: thus with nitrate of lead—

$$Na^4P^2O^7 + 2Pb''N^2O^6 = \overset{''}{Pb}{}^2P^2O^7 + 4NaNO^3;$$

and pyrophosphate of lead decomposed by sulphydric acid, yields **pyrophosphoric acid**; $3H^4P^2O^7$ or $2H^2O.P^2O^5$:

$$\overset{''}{Pb}{}^2P^2O^7 + 2H^2S = H^4P^2O^7 + 2Pb''S.$$

Pyrophosphates are easily converted into metaphosphates and orthophosphates (and vice versâ) by addition or subtraction of water, or a metallic base.

α. The production of a pyrophosphate from an orthophosphate by loss of water has been already mentioned.—β. Conversely, when a pyrophosphate is heated with water or a base, it becomes an orthophosphate: *e. g.*—

$$Na^4P^2O^7 + H^2O = 2Na^2HPO^4$$
$$Na^4P^2O^7 + 2NaHO = 2Na^3PO^4 + H^2O.$$

γ. Pyrophosphoric acid heated to dull redness is converted into metaphosphoric acid: $H^4P^2O^7 - H^2O = 2HPO^3$. The converse reaction is not easily effected, inasmuch as metaphosphoric acid by absorbing water generally passes directly to the state of orthophosphoric acid. Peligot, however, observed the formation of pyrophosphoric from metaphosphoric acid by very slow absorption of water (p. 539).—δ. When a metallic metaphosphate is treated with a proper proportion of a hydrate, oxide, or carbonate, it is converted into a pyrophosphate:

$$2NaPO^3 + \overset{''}{Na}{}^2CO^3 = Na^4P^2O^7 + CO^2.$$

**Fleitmann** and **Henneberg** (Ann. Ch. Pharm. lxv. 304), by fusing together an atom of pyrophosphate of sodium, $Na^3PO^4.NaPO^3$, with two atoms of metaphosphate, $NaPO^3$, obtained a salt having the composition $Na^3PO^4.3NaPO^3 = Na^6P^4O^{12}$, which is soluble without decomposition in a small quantity of hot water, and crystallises from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg obtained another crystallisable but very insoluble salt, having the composition $Na^3PO^4.9NaPO^3 = Na^{12}P^{10}O^{31}$, by fusing together 1 atom of sodic pyrophosphate with 8 atoms of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition (see further **Uelsmann**, Ann. Ch. Pharm. cxviii. 99).

The relative proportions of base and anhydride in these different phosphates is best shown by according to them all the quantity of base contained in the most complex member of the series, that is to say, 6 atoms, as in the following table:

| | |
|---|---|
| Orthophosphate . . . . . . . . | $6M^2O.2P^2O^5 = 4M^3PO^4$. |
| Pyrophosphate . . . . . . . . | $6M^2O.3P^2O^5 = 3M^4P^2O^7$. |
| Fleitmann and Henneberg's Phosphate (*a*) . . | $6M^2O.4P^2O^5 = 2M^6P^4O^{13}$. |
| Fleitmann and Henneberg's Phosphate (*b*) . . | $6M^2O.5P^2O^5 = M^{12}P^{10}O^{31}$. |
| Metaphosphate . . . . . . . . | $6M^2O.6P^2O^5 = 12MPO^3$. |

The several modifications of phosphoric acid and their salts have been examined chiefly by **Berzelius** (Ann. Ch. Phys. [2] ii. 151, 217; x. 278); **Mitscherlich** (*ibid.* xix. 350); **Gay-Lussac** (*ibid.* xli. 331); **Clark** (Ed. J. of Sc. vii. 298); **Stromeyer** (Schw. J. lviii. 123); **Graham** (Phil. Trans. 1833, p. 253; Phil. Mag.

[3] iv. 401); **Maddrell** (Mem. Chem. Soc. iii. 273; Ann. Ch. Pharm. lxi. 53); **Rammelsberg** (Ann. Ch. Pharm. lvi. 210; lxxii. 250; Jahresb. 1847–8, p. 338); **Schwarzenberg** (*ibid.* lxv. 133; Jahresb. 1847–8, p. 345); **Persoz** (Ann. Ch. Pharm. lxv. 163; Jahresb. 1847–8, p. 352); **Fleitmann** and **Henneberg** (Ann. Ch. Pharm. lxv. 304, 387; Jahresb. 1847–8, pp. 354, 357); **H. Rose** (Ann. Ch. Pharm. lxxvi. 2, 13; lxxvii. 319; Jahresb. 1847–8, pp. 231, 351); **Vögeli** (Ann. Ch. Pharm. lxix. 180; Jahresb. 1847–8, p. 694); **Heintz** (Ann. Ch. Pharm. lxviii. 257, 287; lxxii. 264; Jahresb. 1847–8, p. 342; 1849, p. 534); **Raewsky** (Compt. rend. xxvi. 205; Jahresb. 1847–8, p. 240); **Baer** (Ann. Ch. Pharm. lxviii. 255; Jahresb. 1847–8, p. 340); **Werther** (Ann. Ch. Pharm. lxviii. 312; Jahresb. 1847–8, p. 419); **Ludwig** (Jahresb. 1847–8, p. 339; 1849, p. 230; 1852, p. 361); **Fleitmann** (Ann. Ch. Pharm. lxxii. 231; Jahresb. 1849, p. 233); **Reynoso** (Ann. Ch. Pharm. lxxxiii. 98; Jahresb. 1852, p. 318); **Marignac** (Ann. Ch. Pharm. lxxxviii. 232; Jahresb. 1853, p. 339); **Fresenius** (Ann. Ch. Pharm. lxxxvi. p. 216; Jahresb. 1853, p. 322); **Brandes** (Ann. Ch. Pharm. lxxxviii. 272; Jahresb. 1853, p. 381).

**METAPHOSPHORIC ACID**, $HPO^3 = \left.\begin{matrix}P\\H\end{matrix}\right\}O^3 = \left.\begin{matrix}(PO^3)'\\H\end{matrix}\right\}O$, or $H^2O.P^2O^5$.—This acid, discovered by **Graham**, is obtained, as already observed, by acting on phosphoric anhydride with cold water, or by heating orthophosphoric or pyrophosphoric acid to redness. Orthophosphate of ammonium may be substituted for the orthophosphoric acid; but it is difficult to expel the last traces of ammonia. Metaphosphoric acid is also prepared by decomposing some of its salts with another acid, as by exposing the lead-salt suspended in water to a current of sulphydric acid gas.

Metaphosphoric acid in the solid state, as obtained by evaporating its solution and heating the residue to redness, or by boiling ortho- or pyrophosphoric acid to redness, forms a transparent, colourless, glassy, uncrystallisable mass, which dissolves slowly though somewhat abundantly in water, forming a strongly acid liquid. Its solution gives white precipitates with solutions of *albumin, nitrate of silver*, and *chloride of barium*. The last-mentioned precipitate is soluble with difficulty in a large excess of the acid. With *molybdate of ammonium* it gives no precipitate or coloration, until, by the action of the free nitric acid present, it has been fairly converted into orthophosphoric acid.

Metaphosphoric acid is converted slowly at ordinary temperatures, quickly at the boiling heat, into orthophosphoric acid, without passing through the intermediate stage of pyrophosphoric acid. Metaphosphoric acid volatilises completely at a bright red heat, but, according to **H. Rose**, its composition varies during the volatilisation, the last portions volatilised consisting of metaphosphoric acid and phosphoric anhydride; but metaphosphoric acid cannot be completely dehydrated by heat, or indeed by any known process.

***Metaphosphates***, $MPO^3$ or $M^2P^2O^6$.—These salts are produced: 1. By treating the acid with bases.—2. By igniting a monometallic orthophosphate of fixed base, or a dimetallic orthophosphate having one fixed and one volatile base (ammonio-sodic phosphate, for example), or a monometallic pyrophosphate.—3. By double decomposition, the insoluble metaphosphates of silver, lead, and barium, for example, from metaphosphate of sodium, and the ammonium-salt by decomposing metaphosphate of lead with sulphide of ammonium.—4. By heating trimetallic orthophosphates or dimetallic pyrophosphates with the proper proportions of phosphoric anhydride or acid: thus—

$$Na^3PO^4 + P^2O^5 = 3NaPO^3.$$
$$Na^4P^2O^7 + P^2O^5 = 4NaPO^3.$$

Metaphosphates may therefore be regarded as anhydro-salts of orthophosphates and pyrophosphates, a relation further exhibited by the behaviour of sodic or calcic metaphosphate when heated with charcoal, the salt then splitting up into a trimetallic orthophosphate irreducible by the charcoal, and phosphoric anhydride, which is decomposed by the charcoal into carbonic oxide and phosphorus vapour (p. 500).

Metaphosphates of alkali-metals are fusible, soluble salts, not usually crystalline. The metaphosphates are readily decomposed by other acids: thus even acetic acid will decompose metaphosphate of sodium, as shown by the fact that a mixture of acetic acid and metaphosphate of sodium precipitates albumin, although neither reagent separately will produce that effect. The circumstances under which metaphosphates are converted into pyrophosphates and orthophosphates have been already considered.

*Modifications of Metaphosphates.*—The metaphosphates are remarkable for exhibiting very different properties, according to the manner in which they are prepared. These differences are generally attributed to polymeric modifications, the formulæ of which are determined chiefly by the relative numbers of atoms of the two bases contained in the respective double salts.

α. *Hexmetaphosphates*, $M^6P^6O^{18}$.—Ordinary metaphosphoric acid, obtained by the processes above described, forms double salts containing quantities of monatomic metal in the ratio of 5 at. to 1 at., or equivalent quantities of diatomic metal—the calcio-sodic salt, for example, having the composition $\overset{''}{Ca}{}^5Na^2(PO^3)^{12}$, or $2NaPO^3.5Ca''P^2O^6$. The ordinary sodium-metaphosphate, obtained by igniting monosodic orthophosphate and sudden cooling, forms a vitreous mass, the aqueous solution of which gives gelatinous precipitates with the salts of the heavy metals and alkaline earth-metals.

β. *Trimetaphosphates*, $M^3P^3O^9$.—When a considerable quantity of ordinary fused sodic metaphosphate is allowed to cool very slowly, the salt in solidifying acquires a beautifully crystalline structure; and when this mass is digested in a slight excess of warm water, the liquid separates into two layers, the larger stratum containing the crystalline and the smaller stratum the ordinary vitreous salt. The solution of the crystalline variety gives hydrated crystalline precipitates with salts of the heavy metals. The formulæ of the crystalline silver-salt thus produced is $3AgPO^3.H^2O$. The metaphosphoric acid obtained from these salts forms double salts containing 2 at. of one monatomic metal to 1 at. of another, or quantities of diatomic metals equivalent to these.

γ. *Dimetaphosphates*, $M^2P^2O^6$.—When oxide of copper and a slight excess of aqueous phosphoric acid are heated together to 350°, a crystalline powder is formed, insoluble in water, but soluble, with the aid of heat, in sulphuric acid and in ammonia. The corresponding metaphosphates of the alkali-metals, which are obtained by treating the copper-salt with sulphide of potassium, &c., are soluble in water, crystallisable, and converted by heat into insoluble salts. These metaphosphates have a strong tendency to form double salts, all of which contain equal or equivalent numbers of atoms of the two bases. For example, on mixing a concentrated solution of the potassium-salt with chloride of sodium, or of the sodium-salt with chloride of potassium, a crystalline double salt is obtained, having the composition $NaKP^2O^6.H^2O$. Again, concentrated solutions of the ammonium-salt and cupric chloride mixed together, deposit, on addition of alcohol, blue crystalline needles, having the composition $(NH^4)^2Cu''P^4O^{12}.2H^2O$.

δ. *Tetrametaphosphates*, $M^4P^4O^{12}$.—Another variety of metaphosphate is formed by heating phosphoric acid with oxide of lead, bismuth, or cadmium, or with a mixture of 2 at. sodic hydrate and 1 at. cupric oxide. The lead-salt is easily decomposed by alkaline sulphides, and yields the corresponding salts of the alkali-metals. The sodium-salt in combination with water is viscid and elastic, and forms, with a larger quantity of water, a gummy mass, which will not pass through a filter. The double salts of this variety of metaphosphoric acid contain equal or equivalent numbers of atoms of their two bases, like those of the preceding; but as they differ in physical properties, it is probable that they are polymeric with the latter, the sodio-cupric salt, for example, having the composition $Na^4\overset{''}{Cu}{}^2P^8O^{24}$.

ε. *Monometaphosphates*, $MPO^3$.—Lastly, there is a variety of metaphosphates discovered by Maddrell (Mem. Chem. Soc. iii. 373) which are remarkable for their insolubility in water. The potassium-salt is produced by igniting hydrate of potassium and phosphoric acid together in equivalent proportions; the ammonium-salt by heating dimetaphosphate of ammonium to 250°. These metaphosphates are also formed by adding phosphoric acid in excess to solutions of sulphates or nitrates, evaporating to dryness, and heating the residues to 316° or upwards. They are crystalline anhydrous powders. There are no double salts of this variety.

PYROPHOSPHORIC ACID, $H^4P^2O^7 = \left.\begin{matrix}(P^{v})^2\\ H^4\end{matrix}\right\}O^7 = H^3PO^4.HPO^3 = 2H^2O.P^2O^5$.—This acid, discovered by Dr. Clark of Aberdeen, may be prepared by evaporating a solution of orthophosphoric acid till its temperature rises to 215°, but the product is always somewhat contaminated with unchanged orthophosphoric acid. A purer product is obtained by decomposing pyrophosphate of lead with sulphydric acid, and evaporating the filtrate till it attains the temperature above mentioned. As thus prepared it forms a soft glass. Peligot, however, found (Ann. Ch. Phys. [2] lxxiii. 286) that fused phosphoric acid (metaphosphoric acid), left to itself in a bottle for several years, during which time it absorbed water, formed at the top transparent crystals of orthophosphoric acid, in the middle a mother-liquid of specific gravity 1·7, and at the bottom, opaque indistinct crystals of pyrophosphoric acid resembling loaf-sugar.

Pyrophosphoric acid is converted into metaphosphoric acid when heated to redness, and into orthophosphoric acid when boiled with water. The last conversion takes place also at ordinary temperatures, but very slowly, so that the aqueous acid may be kept unaltered for even half a year (Graham). Pyrophosphoric acid in aqueous solution does not precipitate *albumin*, *chloride of barium*, or *nitrate of silver*, but after neutralisation it gives white precipitates with the last two reagents.

*Pyrophosphates.*—Pyrophosphoric acid being tetrabasic is capable of forming four classes of salts, three acid and one neutral, represented, in the case of monatomic metals, by the formulæ:

$$MH^3P^2O^7,\quad M^2H^2P^2O^7,\quad M^3HP^2O^7,\quad \text{and}\quad M^4P^2O^7.$$

The neutral pyrophosphates may be produced, as already observed, by igniting dimetallic orthophosphates; also, by neutralising the acid with bases, or by heating any form of phosphoric acid, or a metaphosphate, with a quantity of oxide, hydrate or carbonate, sufficient to furnish the required quantity of base: *e. g.*—

$$\begin{aligned} 2HPO^3 + 2Na^2CO^3 &= Na^4P^2O^7 + 2CO^2 + H^2O. \\ 2NaPO^3 + 2NaHO &= Na^4P^2O^7 + H^2O. \end{aligned}$$

Acid pyrophosphates may be prepared by neutralising one quantity of the acid with a base and adding thereto one-third, or one, or three more proportions of acid.

Many pyrophosphates are formed by double decomposition. Solutions of pyrophosphates, even when much diluted, give precipitates with salts of *calcium*, *barium*, *lead*, and *silver*. The precipitates formed by sodic pyrophosphate in solutions of *copper*, *nickel*, and some other metals, are double salts, containing 2 at. sodium to 3 at. of the diatomic metal (p. 237): *e. g.*—

$$2Na^4P^2O^7 + 3Cu''Cl^2 = \overset{''}{Cu}{}^3Na^2P^4O^{14} + 6NaCl.$$

This constitution is exhibited by most of the double pyrophosphates, and seems to favour the notion that these salts are compounds of orthophosphates and metaphosphates: thus, $Cu^3Na^2P^4O^{14} = Cu^3P^2O^8.2NaPO^3$.

Among neutral pyrophosphates, those of the alkali-metals only are soluble in water; their solutions have a slight alkaline reaction, and cannot be boiled without conversion into orthophosphates. The other salts are soluble in acids, and generally in an excess of sodic pyrophosphate, forming the double salts just mentioned, which exhibit a peculiar behaviour with reagents. Thus, from a solution of ferric or manganous pyrophosphate in pyrophosphate of sodium, the heavy metal can scarcely be precipitated by sulphydric acid or sulphide of ammonium. The insoluble pyrophosphates are soluble also in excess of the heavy metallic salt from which they are precipitated; the solution is precipitated by heat, and the precipitate is not redissolved on cooling—as is the case with orthophosphates under similar circumstances. The alkaline-earthy pyrophosphates dissolve with difficulty in acetic acid.

When a pyrophosphate containing a metal reducible from its oxide by heat alone is ignited in a stream of *hydrogen*, the metal is reduced, and water, phosphoric acid, and other phosphorus-compounds are separated; if the oxide is irreducible by itself, but reducible by hydrogen, a metallic phosphide is formed, while water and various phosphorus-compounds escape; if the oxide is not reducible by hydrogen, the pyrophosphate is resolved into an orthophosphate and phosphoric anhydride ($3M^4P^2O^7 = 4M^3PO^4 + P^2O^5$), which latter is partly decomposed into phosphorous acid, phosphoretted hydrogen, and red phosphorus. (Struve, J. p. Chem. lxxix. 345.)

The other reactions by which pyrophosphates are converted into ortho- and metaphosphates have been already considered.

**ORTHOPHOSPHORIC ACID**, $H^3PO^4 = \left.\begin{matrix}P^v\\H^3\end{matrix}\right\}O^4 = \left.\begin{matrix}(PO)'''\\H^3\end{matrix}\right\}O^3$, or $3H^2O.P^2O^5$.—This acid is produced, as already observed: 1. By the action of boiling water on phosphoric anhydride, metaphosphoric acid, or pyrophosphoric acid.—2. By the combustion of phosphoretted hydrogen in air or oxygen.—3. By the oxidation, spontaneous or otherwise, of hypophosphorous and phosphorous acids.—4. By oxidising phosphorus with nitric or hypochlorous acid.—5. By decomposing its salts with acids, tricalcic phosphate (bone-earth) for example, with sulphuric acid, or phosphate of lead with sulphydric acid.—6. By the action of water on phosphoric oxychloride:

$$PCl^3O + 3H^2O = H^3PO^4 + 3HCl.$$

Pentachloride of phosphorus, acted upon by a small quantity of water, yields phosphoric oxychloride:

$$PCl^5 + H^2O = 2HCl + PCl^3O,$$

which may be converted by a larger quantity of water into phosphoric acid.

*Preparation.*—1. *By the action of Nitric Acid on Phosphorus.*—One part of phosphorus is heated in a retort with about 15 pts. of dilute nitric acid of specific gravity 1·2 until it is dissolved. The distillate which contains some phosphorous acid is then returned to the retort, and the entire liquid is evaporated down. At a certain degree of concentration, a very considerable effervescence occurs, due to the oxidation of the phosphorous acid into phosphoric acid. Small quantities of nitric acid are then added from time to time, until the last addition no longer produces effervescence, after which the liquid is evaporated to expel the nitric acid. If the evaporation is carried so far as to produce pyrophosphoric or even metaphosphoric acid, the residue is to be boiled for a short time in water, whereby these last two acids are reconverted into orthophosphoric acid.

2. *From Bone-ash.*—Bone-ash is decomposed by sulphuric acid, as described on page 500, and the acid solution filtered from the insoluble gypsum is concentrated to a small bulk and mixed with more sulphuric acid, whereby a further precipitate of gypsum is formed, which after dilution with water is separated by straining through linen. This operation of evaporation to a small bulk, treatment with sulphuric acid, dilution with water, and filtration, is repeated a second and even a third time, till the lime is completely removed. The acid is next evaporated to a syrup, and gently ignited to expel the sulphuric acid. The residue, which still contains magnesia and soda, derived from the bone-ash, is freed from the greater part of these impurities by solution in boiling water, concentration, and heating for about half an hour to 315°. A white powder then separates, consisting of sodio-magnesic metaphosphate, $3Mg''P^2O^6.2NaPO^3$. The syrupy mass is left to cool, afterwards dissolved in cold water, and the liquid is filtered. The filtrate when boiled constitutes a solution of orthophosphoric acid, contaminated with a trace of sodium, but otherwise pure. To obtain a perfectly pure phosphoric acid, recourse must be had either to the oxidation of phosphorus with nitric acid or to the following process.

3. *From Pentachloride of Phosphorus.*—Chlorine is passed in excess through phosphorus melted under water, whereby pentachloride of phosphorus is produced, and immediately decomposed by the water into hydrochloric and orthophosphoric acids:

$$PCl^5 + 4H^2O = H^3PO^4 + 5HCl.$$

The phosphoric acid may be freed from hydrochloric acid by ebullition.

*Properties.*—Orthophosphoric acid may be obtained in hard, transparent, prismatic crystals, by concentrating its solution to a thin syrup, and then allowing it to stand for some time over oil of vitriol.

According to Schiff (Ann. Ch. Pharm. cxiii. 183), the specific gravity of the aqueous solution varies with its strength in the manner shown by the following table:

| Percentage of $H^3PO^4$. | Specific gravity at 15°. | Percentage of $H^3PO^4$. | Specific gravity at 15°. |
|---|---|---|---|
| 6 | 1·0333 | 24 | 1·1463 |
| 12 | 1·0688 | 36 | 1·2338 |
| 18 | 1·1065 | 54 | 1·3840 |

The aqueous solution may be heated to 160° without altering the character of the acid; but at 213° it is converted principally into pyrophosphoric acid, while above this temperature metaphosphoric acid begins to be formed, and, after the application of a full red heat, constitutes the entire residue.

Aqueous orthophosphoric acid has a strong acid reaction, and at a boiling heat decomposes the salts of most volatile acids. It does not precipitate solutions of albumin, chloride of barium, nitrate of silver, or ferric chloride, until completely or partially neutralised, when it gives the reactions presently to be described.

*Orthophosphates.*—$MH^2PO^4$ and $M''H^4P^2O^8$, *monometallic* or *diacid salts*; $M^2HPO^4$ and $M''HPO^4$, *dimetallic* or *monoacid salts*; $M^3PO^4$, $\overset{''}{M}{}^3P^2O^8$, and $M'''PO^4$, *trimetallic, neutral,* or *normal salts.* There are also superbasic orthophosphates, many of which occur as natural minerals—*e.g.* green ironstone, $Fe'''PO^4.Fe'''H^3O^3$; turquois, $Al'''PO^4.Al'''H^3O^3.H^2O$.

Many other phosphates are also found in nature, though rarely in a state of purity; they frequently occur mixed in various proportions with arsenates, with which they are isomorphous. Several native phosphates are found in combination with fluorides or chlorides—the *apatites* and *wagnerites*, for example. H. Deville and Caron (Ann. Ch. Pharm. cix. 242) have prepared crystallised compounds of this kind by igniting a trimetallic phosphate with an excess of the corresponding chloride or fluoride, and washing out the excess of the chloride or fluoride from the crystallised compound, which separates on cooling.

The phosphates of the alkali-metals are usually prepared by treating phosphoric acid or dicalcic phosphate (superphosphate of lime) with alkaline hydrates or carbonates. Dicalcic phosphate boiled with solution of sodic carbonate yields the ordinary disodic phosphate, and from this the monosodic and trisodic salts are obtained by the addition of phosphoric acid and caustic soda respectively. The potassium and ammonium-salts may be prepared in a similar manner. Insoluble phosphates are prepared by precipitating soluble salts of the respective metals with alkaline phosphates.

Among trimetallic phosphates, those only of the alkali-metals are soluble in water. The solutions have a strong alkaline reaction, whence these salts were formerly called *basic phosphates:* they are decomposed even by carbonic acid, producing mixtures of alkaline carbonate and dimetallic phosphate: *e.g.*—

$$Na^3PO^4 + H^2CO^3 = Na^2HPO^4 + NaHCO^3.$$

Among dimetallic phosphates, those of the alkali-metals are soluble in water. They are often called *neutral phosphates,* though their solutions have a feebly alkaline reaction. The remaining dimetallic phosphates are unstable, and generally insoluble compounds, which have a strong tendency to decompose into soluble monometallic and insoluble trimetallic salts.

The monometallic phosphates are all soluble in water, forming strongly acid solutions. Most trimetallic phosphates dissolve to a greater or less extent in aqueous phosphoric, nitric, and hydrochloric acids, being probably converted at the same time into monometallic salts; but monometallic phosphates of the heavy metals are not, except in a few instances, known as definite compounds.

Under ordinary circumstances the heavy metals, silver and lead for instance, form only one class of orthophosphates, viz. the trimetallic phosphates; consequently, when a solution of a monometallic or dimetallic phosphate of alkali-metal, which is either neutral or slightly alkaline to test-paper, is added to a perfectly neutral solution of nitrate of silver, or other heavy metallic salt, a precipitate of trimetallic phosphate is produced, and free acid passes into the solution, so that the liquid acquires a strong acid reaction; *e. g.*—

$$NaH^2PO^4 + 3AgNO^3 = Ag^3PO^4 + NaNO^3 + 2HNO^3.$$
$$Na^2HPO^4 + 3AgNO^3 = Ag^3PO^4 + 2NaNO^3 + HNO^3.$$

*Reactions.*—1. Soluble orthophosphates give with *nitrate of silver* a lemon-yellow precipitate of triargentic phosphate, $Ag^3PO^4$, soluble in nitric acid and in ammonia.

2. With *acetate* or *nitrate of lead* they form a white precipitate of triplumbic phosphate, $\overset{''}{Pb}{}^3P^2O^8$, insoluble in ammonia and acetic acid, soluble in nitric acid. If a chloride is present, the precipitate contains chloride of lead chemically combined with the phosphate. Phosphate of lead fused before the blowpipe forms a crystalline bead on cooling.

3. With the *chlorides of barium* and *calcium*, orthophosphates give white precipitates of dimetallic phosphates, $Ba''HPO^4$ and $Ca''HPO^4$, easily soluble in nitric, hydrochloric, and acetic acid.

4. With *sulphate* or *chloride of magnesium*, to which ammonia and chloride of ammonium have been added, they give a white crystalline precipitate of ammonio-magnesian phosphate, $(NH^4)^2Mg^2P^2O^8.12H^2O$, easily soluble in all acids, slightly soluble in pure water, but absolutely insoluble in water containing free ammonia, even in presence of excess of ammoniacal salts. In very dilute solutions the precipitate forms very slowly; its deposition is accelerated by scratching with a glass rod the inside of the vessel containing the solution.

5. With *ferric chloride*, soluble orthophosphates give a yellowish-white precipitate of ferric phosphate, $Fe'''PO^4$, soluble in hydrochloric acid, in excess of ferric chloride, in ferric acetate, and in ammonia, but absolutely insoluble in acetic acid; so that it forms when acetate of sodium is added to its solution in hydrochloric acid, or when acetate of sodium and a little ferric chloride are added to the solution of an alkaline-earthy phosphate.*

6. *Uranic nitrate* behaves with soluble orthophosphates in the same manner as ferric salts.

7. *Mercurous nitrate* gives with soluble orthophosphates a white precipitate easily soluble in nitric acid. If the solution of any orthophosphate in excess of nitric acid is evaporated over the water-bath to complete dryness with excess of metallic mercury, and the dry residue (which contains no free acid) is treated with water, all the metals contained in the phosphates are dissolved as nitrates, while the whole of the phosphoric acid remains undissolved as mercurous phosphate. This reaction is employed by H. Rose, for the separation of phosphoric acid from all metals except mercury.

8. With *nitrate of bismuth*, soluble orthophosphates give a white precipitate of bismuth-phosphate, $Bi'''PO^4$, insoluble in dilute nitric acid.

9. When a solution of *molybdate of ammonium* is added to the solution of any orthophosphate containing free nitric acid, and the whole is heated, the solution immediately turns yellow, and a bright yellow precipitate of phosphomolybdate of ammonium is formed either immediately or after some time. This precipitate is insoluble in acids, soluble in ammonia or in excess of the phosphate; hence this reaction is peculiarly fitted for the detection of small traces of phosphoric acid (as in minerals, soils, or the deposits from mineral springs).

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* Arsenic acid exhibits this reaction as well as phosphoric acid; and aluminium-salts are precipitated under the same circumstances, though not so completely as ferric salts.

For the detection of orthophosphoric acid in neutral or alkaline solutions, *chloride of ammonium*, *ammonia*, and a *magnesium-salt* are generally employed—in an acid solution, *ferric chloride* and *acetate of sodium*. The most delicate reagent of all is *molybdate of ammonium*. Arsenic acid, which exhibits all these reactions, is easily distinguished from phosphoric acid, and if present may be entirely removed, by passing sulphydric acid gas through the solution previously mixed with sulphurous acid (i. 538). Metaphosphoric and pyrophosphoric acids are distinguished from orthophosphoric acid by their reaction with nitrate of silver (the former also by its property of coagulating albumin, p. 536); also by molybdate of ammonium, with which they do not produce any yellow precipitate or coloration until they are converted by the free nitric acid present into orthophosphoric acid.

Trimetallic orthophosphates of fixed bases are not at all decomposed by ignition; dimetallic and monometallic phosphates are converted by ignition into pyrophosphates and metaphosphates respectively. The trimetallic phosphates of alkali-metals and alkaline earth-metals are not decomposed by ignition with *charcoal*, but the mono- and dimetallic phosphates of these bases are decomposed into trimetallic phosphates and free phosphorus (p. 500). The trimetallic phosphates of the heavy metals, on the contrary, are decomposed by ignition with charcoal, generally yielding metallic phosphides; but the lead-salt yields metallic lead and phosphorus-vapour. The several phosphates of magnesium when heated with charcoal give off phosphorus and leave magnesia. *Potassium* or *sodium* heated with phosphates effects a reduction of the salts and formation of a phosphide of the alkali-metal, which gives off phosphoretted hydrogen when moistened with water. The alkaline-earthy phosphates are only partially decomposed by fusion with an *alkaline carbonate*, while most other insoluble phosphates (*e.g.* those of magnesium, zinc, copper, manganese, and iron) are completely decomposed by this means; the fused mass always contains orthophosphoric acid. By boiling in a solution of caustic alkali or alkaline carbonate the insoluble phosphates are only partially or not at all decomposed. Phosphate of aluminium can only be decomposed (in the dry way) by fusion with its own weight of silica, and six times its weight of sodic carbonate.

### *Quantitative Analysis of Phosphates: Estimation and Separation of Phosphoric Acid.*

1. *Estimation by means of Lead-oxide.*—When phosphoric acid exists in a solution containing no fixed base, and no other acid except nitric acid, it may be estimated by adding a known weight of lead-oxide, then evaporating and calcining in the manner already described for the estimation of hypophosphorous acid (p. 524). This method is directly applicable to the estimation of phosphoric acid in all its modifications.

2. *By precipitation as Ammonio-magnesian Phosphate.*—The precipitation of orthophosphoric acid from an aqueous solution in which it exists in the free state or combined with an alkali, is best effected by the addition of sulphate of magnesium and excess of ammonia, chloride of ammonium being likewise added to prevent the precipitation of magnesia in the form of hydrate. The phosphoric acid is then precipitated as ammonio-magnesian phosphate, $(NH^4)^2Mg^2P^2O^8$. The precipitate does not settle down at once, but its deposition may be accelerated by leaving the vessel in a warm place. Care must be taken, however, not to allow the liquid to become very hot, as in that case hydrate of magnesium will be precipitated, and will be very difficult to redissolve. The precipitate, after standing for about two hours, is collected on a filter and washed with water containing ammonia, as pure water decomposes it. It is then dried and ignited, whereby it is converted into pyrophosphate of magnesium, $Mg''O.P^2O^5$ or $Mg^2P^2O^7$, containing 63·67 per cent. of phosphoric anhydride, $P^2O^5$, and 27·98 per cent. of phosphorus.

If the phosphoric acid is in the state of meta- or pyrophosphoric acid, it must first be converted into the orthophosphoric acid by fusing the salt with five or six times its weight of carbonate of sodium, or, better, with a mixture of carbonate of potassium and carbonate of sodium in equivalent proportions, which fuses at a much lower temperature. By this fusion with excess of an alkaline carbonate the phosphoric acid is in most cases completely separated from any other base with which it may be combined, and converted into a tribasic phosphate of the alkali-metal, which may then be treated as above. The conversion may also be effected by prolonged boiling with water, acids, or alkalis.

3. *As Phosphate of Bismuth.*—In a solution free from sulphuric or hydrochloric acid, phosphoric acid may be correctly estimated by precipitation with nitrate of bismuth. The precipitate consists of bismuth-phosphate, $Bi'''PO^4$ or $Bi^2O^3.P^2O^5$, containing 23·28 per cent. $P^2O^5$. Pyrophosphoric acid is also completely precipitated by nitrate of bismuth, the precipitate $2Bi^2O^3.3P^2O^5$ containing 31·28 per cent. $P^2O^5$; metaphosphoric acid must be converted into orthophosphoric acid by boiling with nitric acid. Sulphuric and hydrochloric acids, if present, must be removed by precipitation with chloride of barium and

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nitrate of silver respectively, the excess of silver in the latter case being then precipitated by sulphydric acid. If the solution contains iron in the state of ferric salt, the phosphate of bismuth is but slowly precipitated, and always contains iron, but this source of error may be obviated by reducing the ferric oxide to ferrous oxide (best with sulphydric acid); the process is thus rendered available for the estimation of phosphoric acid in soils, coprolites, iron ores, &c. (Chancel, Compt rend. l. 416; li. 882). According to M'Curdy, Brush, and Johnson, however (Sill. Am. J. [2] xxxi. 281; Jahresh. 1861, p. 823), the alumina in such substances introduces a similar error; and the process is likewise inapplicable to solutions containing chromic or uranic oxide.

4. *Estimation by means of Stannic Oxide.*—This method, first proposed by Reynoso (Ann. Ch. Pharm. lxxx. 354; Jahresb. 1851, p. 613), depends on the insolubility of stannic phosphate in nitric acid. A known weight of pure tin-foil, and the substance in which the phosphoric acid is to be determined, are treated simultaneously with an excess of nitric acid; the liquid is filtered as soon as the tin is completely oxidised, and the residue is washed, dried, and calcined. Its weight, diminished by that of the stannic oxide formed from the weight of tin employed, gives the quantity of phosphoric anhydride present. The nitric acid solution contains all the bases present.

In calcining the stannic phosphate, care must be taken to allow free access of air, as otherwise part of the stannic oxide may be reduced by the carbonaceous matter of the filter or of the flame; to avoid such sources of error, it is best to moisten the mass with nitric acid before calcining. It is also necessary that the tin be quite pure and added in considerable excess, equal to eight or ten times the weight of the phosphoric acid to be estimated.

A modification of this method proposed by Reissig (Ann. Ch. Pharm. xcviii. 339; Jahresb. 1856, p. 726) consists in dissolving the washed precipitate of stannic phosphate in caustic potash, diluting with water, saturating with sulphydric acid, and adding an excess of acetic or dilute sulphuric acid, which precipitates the tin as stannic sulphide. The phosphoric acid remains dissolved, and may be precipitated from the filtrate as ammonio-magnesian phosphate.

*Precipitation by Uranic salts.*—This method, first proposed by Leconte (Compt. rend. xxix. 55; Jahresb. 1849, p. 572; 1853, p. 642), and afterwards modified by Arendt and Knopp (J. pr. Chem. lxx. 385; Jahresb. 1856, p. 728), consists in precipitating the phosphoric acid by a solution of uranic acetate. This solution, prepared by precipitating uranic nitrate or chloride with ammonia, and dissolving the precipitate in acetic acid, without previous filtration, is added to the solution containing the phosphoric acid, which, if it contains inorganic acids (it is best to dissolve the phosphate in nitric or hydrochloric acid), should be previously mixed with acetate of sodium. On heating the mixture, a yellow precipitate is formed, consisting of ammonio-uranic phosphate, which is reduced by ignition to uranic pyrophosphate, $2U^2O^3.P^2O^5$. The bases previously combined with the phosphoric acid remain in solution, the phosphates of diatomic metals, barium, calcium, magnesium, &c., being easily decomposed in this manner, and even aluminic and ferric phosphates being decomposed by prolonged heating with a large excess of uranic acetate in presence of acetate of ammonium and free acetic acid; but the method is not much used, on account of the great difficulty of thoroughly washing the precipitate of ammonio-uranic phosphate.

6. *Estimation by means of Ferric salts.*—This method, proposed by Berthier, consists in adding to the solution of the phosphate a solution of ferric nitrate or chloride containing a known quantity of iron (best prepared by dissolving a known weight of clean iron-wire in nitro-muriatic acid), and precipitating by ammonia. The precipitate, consisting of ferric phosphate with excess of ferric oxide, is carefully washed with hot water, then dried and ignited; its weight, diminished by that of the ferric oxide produced from the known weight of iron, gives the quantity of phosphoric anhydride present.

It is important to use an excess of iron (at least, 1 pt. of iron to 2 pts. of phosphoric anhydride to be estimated), otherwise a phosphate of iron will be formed which dissolves in ammonia. But even when the proper quantity of iron is added, there is still a loss of ferric oxide during the washing of the precipitate, the wash-water, whether pure water or water containing ammonia be used, being always more or less coloured: hence this method, in the form above described, cannot be depended upon when great accuracy is required. For the precipitation of pyrophosphoric acid, a still larger quantity of iron is required than for orthophosphoric acid.

Much more exact results are obtained by nearly neutralising the liquid containing the phosphoric acid and the ferric salt with an alkali or alkaline carbonate, then adding a considerable quantity of *sodic acetate*, and boiling. The whole of the phosphoric acid and iron are thereby precipitated as basic ferric phosphate, mixed with basic ferric acetate, while the solution becomes perfectly colourless, and does not retain a trace of iron. The liquid is then to be boiled, filtered while still hot, and washed with boiling water containing a little acetate of ammonium. The washed precipitate is dried and calcined in a platinum crucible, the residue then moistened with a little nitric acid, heated again and weighed, and the quantity of phosphoric anhydride calculated as before. The method thus modified may be used for the separation of phosphoric acid from baryta, strontia, lime, and magnesia.

Another modification of Berthier's method introduced by Kobell (J. pr. Chem. xxxvi. 301; Jahresb. 1849, p. 566) consists in precipitating the solution of phosphoric acid and ferric oxide with *carbonate of barium* instead of ammonia. The washed and dried precipitate is weighed, then dissolved in hydrochloric acid, and the barium is precipitated by sulphuric acid. The weight of barytic sulphate thus obtained gives, by calculation, the quantity of barytic carbonate added; and this weight, together with that of the ferric oxide deducted from the total weight of the precipitate, gives the quantity of phosphoric anhydride. This method may be used for the separation of phosphoric acid from all bases which are not precipitated by carbonate of barium.

7. *By Ceric salts.*—A solution of ceric nitrate or sulphate produces in the nitric acid solution of any phosphate, *e.g.* calcic, ferric, uranic, or aluminic phosphate, a white or slightly yellowish precipitate of ceric phosphate of constant composition and insoluble in the acid liquid. (Damour and H. Deville, Instit. 1858, p. 69; Jahresb. 1858, p. 593.)

*Volumetric Methods.*—The volumetric process most generally used for the estimation of phosphoric acid is that of Liebig, which depends upon the insolubility of ferric phosphate in acetic acid. The solution containing the phosphoric acid is mixed with acetic acid or acetate of sodium, according as it is neutral or acid; and a solution of ferric chloride or ammonio-aluminic sulphate (ammonia-alum) of known strength is added, in quantity just sufficient to precipitate the whole of the phosphoric acid as ferric phosphate ($Fe^2O^3.P^2O^5$ or $Fe'''PO^4$). The chief difficulty in this process is to determine the moment when the precipitation is complete. For this purpose, Liebig places a drop of solution of ferrocyanide of potassium on a piece of white filter-paper, leaves it to spread, then lays another piece of filter-paper over the first, and places on it a drop of the liquid to which the ferric phosphate has been added. This liquid, in passing through the paper, parts with the ferric phosphate which it holds in suspension, before it comes in contact with the solution of ferrocyanide on the lower piece of paper: hence no blueing of the latter will take place, unless the liquid contains an excess of ferric chloride. The addition must, therefore, be continued till a faint blueing of the ferrocyanide just begins to take place. This method is used by Liebig for the estimation of phosphoric acid in urine.

Raewsky (Jahresb. 1847–8, p. 945) adds an excess of the ferric solution, collects the precipitated ferric phosphate on a filter; dissolves it, after washing, in hydrochloric acid; and determines the quantity of iron in it by Margueritte's method with permanganate of potassium (i. 263); and thence calculates the quantity of phosphoric acid from the formula $Fe'''PO^4$.

### *General Methods of separating Phosphoric Acid from Bases.*

*a. By Mercurous Nitrate.*—This reaction, already mentioned (p. 542), affords the means of separating phosphoric acid from all bases whatever. The phosphate, or mixture of phosphates, being dissolved in nitric acid, the solution may either be evaporated to dryness in contact with metallic mercury, or exactly neutralised with caustic potash or soda, and then mixed with mercurous nitrate, which throws down the mercury as mercurous phosphate.

In most cases the first of these methods is to be preferred. The solution of the phosphate in nitric acid is placed in a porcelain basin, and pure metallic mercury is added, in such quantity that a small portion may remain undissolved by the nitric acid. The liquid is then evaporated to complete dryness over a water-bath, so as to expel the whole of the free nitric acid; and the residue is treated with water, which dissolves all the bases as nitrates, leaving the phosphoric acid undissolved as mercurous phosphate. This salt, after drying, is mixed in a platinum crucible with an excess of dry carbonate of sodium, or, better, of a mixture of potassic and sodic carbonates in equivalent proportions; and heated over a lamp, first to a temperature below redness, and not sufficient to fuse the mass, till all the metallic mercury and all the mercury-salts excepting the phosphate, are expelled—then to the highest temperature obtainable by the gas-flame. The mercurous phosphate is thereby decomposed, the mercury being expelled and an alkaline phosphate produced. This when cold is dissolved in water, and the phosphoric acid precipitated as ammonio-magnesian phosphate.

This method gives very exact results, provided care be taken to dry the residue obtained on evaporating the nitric acid solution very completely, so that no free nitric acid may remain to hold any of the original phosphate in solution, and in fusing the mercurous phosphate with alkaline carbonate, to regulate the heat very carefully in the manner above described, so as to avoid loss by spirting. When properly carried out, it is regarded by **Rose** as the best of all methods of separating phosphoric acid from bases. It is moreover applicable in the manner just described to the analysis of all phosphates excepting those of iron (ferricum) and aluminium, in which cases it requires certain modifications. The nitrates of these bases when evaporated, even at the heat of the water-bath, give off part of their nitric acid, and are thereby rendered to a great extent insoluble in water, so that when their nitric acid solution is evaporated in contact with metallic mercury, and the residue treated with water, a small portion only of the iron or aluminium passes into the aqueous solution, the larger portion remaining undissolved, together with the mercurous phosphate. In the case of iron the process requires but little alteration, tor when the dried residue is ignited with the alkaline carbonate, the ferric phosphate is completely decomposed; so that, on treating the fused mass with water, the whole of the phosphoric acid passes into solution as before, while the iron remains as ferric oxide, and its amount may be added to that which has passed into solution as nitrate. In the case of aluminium, however, the process in this form is no longer applicable, for aluminic phosphate is but very imperfectly decomposed by fusion with alkaline carbonates. In this case, therefore, it is necessary to adopt the second form of the process above mentioned, which consists in precipitating the neutralised solution of the phosphate in nitric acid with mercurous nitrate, separating the precipitated mercurous phosphate by filtration, washing it with water containing a little mercurous nitrate, and decomposing it when dry by fusion with alkaline carbonate, as above. The filtrate contains all the aluminium, together with the excess of mercurous salt. The greater part of the mercury is precipitated from it by hydrochloric acid; a smaller portion, which has passed into the state of mercuric salt and still remains dissolved, is separated by sulphydric acid; and in the remaining solution the aluminium is determined by the usual methods. If any of the alkaline earths are also present, especially lime, this last mode of separation cannot be applied, because a small quantity of earthy phosphate is then precipitated, together with the mercurous phosphate.

For full details of the preceding process, see **H. Rose.** (*Traité de Chimie Analytique*, ii. 708.)

β. *By Nitrate of Silver or Nitric Acid and Metallic Silver.*—The mode of proceeding is similar to that with mercurous nitrate, excepting that when the phosphoric acid is precipitated from the neutralised solution by nitrate of silver, the phosphate of silver must be collected on a tared filter, and weighed after drying at 100°.

7. *Precipitation by Molybdate of Ammonium.*—The molybdic solution is prepared by dissolving 1 pt. of molybdic trioxide in 8 pts. of strong aqueous ammonia, and mixing the solution with 20 pts. of nitric acid. This liquid is added to the solution of the phosphate in nitric acid, in such proportion that the quantity of molybdic trioxide may be thirty or forty times as great as that of the phosphoric acid to be determined. The liquid, together with the resulting yellow precipitate, is digested for several hours at a rather high temperature, and the precipitate is washed on a filter with the liquid which has been used for the precipitation. The yellow precipitate is then dissolved off the filter by ammonia, and the phosphoric acid is precipitated from the filtrate as ammonio-magnesian phosphate.

This method serves for the separation of phosphoric acid from the alkaline earths, the other earthy oxides, and likewise from alumina, ferric oxide, and many other metallic oxides; but it cannot be depended upon for giving exact results, excepting when the quantity of phosphoric acid to be determined is very small. Pyrophosphoric and metaphosphoric acids, to be determined by this method, must first be converted into orthophosphoric acid by prolonged boiling with nitric acid.

**Lipowitz** (Pogg. Ann. cix. 135; Jahresb. 1860, p. 700) dissolves 2 pts. molybdic trioxide in a warm solution of 1 pt. tartaric acid in 15 pts. water; adds 10 pts. aqueous ammonia of specific gravity 0·97, and 15 pts. nitric acid; heats the whole to boiling; filters from a small quantity of molybdic trioxide which separates; and uses the resulting solution for the quantitative estimation of phosphoric acid by direct precipitation. For this purpose a quantity of the solution (about 5 or 6 c.c. to 0·05 grm. phosphoric anhydride, to be determined) is heated to boiling in a porcelain dish, the acidulated solution of the phosphate is added, the yellow precipitate is collected on a weighed filter, washed with water containing $\frac{1}{50}$th of nitric acid, and dried at 20°—30°, or better, over oil of vitriol, and weighed. It contains, according to Lipowitz, 3·607 per cent. $P^2O^5$.

It must be observed, however, that the yellow precipitate is soluble in a large quantity of tartaric acid. (**H. Rose.**)

γ. *By Sulphuric Acid and Alcohol.*—As many sulphates, especially those containing strong bases, are insoluble in alcohol, the separation of phosphoric acid from the corresponding bases may be effected by mixing the solution of the phosphate in water,

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nitric acid, or hydrochloric acid, with sulphuric acid and with alcohol—the base being then precipitated as sulphate, while the phosphoric acid remains dissolved in the alcohol. This method is found, however, to give exact results only when applied to the phosphates of the alkaline earth-metals and phosphate of lead. With other bases an error of 4 per cent. sometimes arises, even when the analysis is performed with all possible care, and ether is added as well as alcohol.

δ. *By fusion with Alkaline Carbonates.*—Many phosphates are completely decomposed by fusion with excess of alkaline carbonate, a mixture of potassic and sodic carbonates in equivalent proportions being the most convenient for the purpose. The phosphates of the heavy metals are for the most part easily decomposed in this manner, but the phosphates of the alkaline earth-metals, and especially phosphate of calcium, are but imperfectly decomposed thereby, and must therefore be treated by other methods. The decomposition by fusion with alkaline carbonate, when it can be applied, is especially convenient for the analysis of phosphates mixed with sulphates, chlorides, and other salts, the several acids passing, together with the phosphoric acid, into the state of alkaline salts.

ε. *By Tartaric or Citric Acid.*—The precipitation of many metals from solutions of their salts by alkalis, is prevented by the presence of certain fixed organic substances, tartaric and citric acid among the number. Hence the separation of phosphoric acid from such bases may be effected by adding to the solution of the phosphate a considerable quantity of tartaric or citric acid, then an excess of ammonia, sal-ammoniac, and sulphate of magnesium. The phosphoric acid is then precipitated as ammonio-magnesian phosphate, while the bases remain in solution. When tartaric acid is used, as originally proposed by Otto, a small quantity of tartrate of magnesium is frequently precipitated, together with the ammonio-magnesian phosphate, and is difficult to get rid of: hence R. Warington, Jun. (Chem. Soc. J. xvi. 304), recommends the use of citric acid, which does not introduce this source of error. Sometimes a small quantity of the base is precipitated, together with the phosphate, in spite of the presence of the organic acid. To guard against this source of error, it is best to redissolve the precipitate in hydrochloric acid, again add citric acid, and supersaturate with ammonia. The ammonio-magnesian salt is then reprecipitated in a state of perfect purity.

This method is employed chiefly for the separation of phosphoric acid from ferric oxide and alumina. From the liquid filtered from the precipitated phosphate, iron is precipitated by sulphide of ammonium; but aluminium, which is precipitated by this reagent, not as sulphide but as hydrate, cannot be separated thereby, or by ammonia or alkaline carbonates, from the solution under consideration, on account of the organic matter present. To effect its separation, the solution is mixed with a quantity of sodic carbonate sufficient to decompose all the chloride of ammonium present, then evaporated to dryness; and the residue is ignited to burn away the greater part of the organic matter, then digested in hydrochloric acid, which dissolves part of the alumina and all the magnesia present, leaving a mixture of alumina and charcoal. This residue is either calcined a second time, to burn away the remaining charcoal, or, better, it is fused with a mixture of nitre and alkaline carbonate. In the latter case the alkaline salts may be dissolved out by water, leaving a residue of alumina easily soluble in hydrochloric acid. In the former, the alumina is left in a difficultly soluble state, and to render it soluble it must be fused with acid sulphate of potassium; the fused mass then dissolves completely in water. The solution of alumina thus obtained is added to the other portion, and the alumina precipitated by ammonia in the usual manner. The decomposition of the chloride of ammonium before calcination is essential, because that salt in volatilising would carry with it a portion of the aluminium in the form of chloride.

ζ. *By Carbonate of Barium.*—The separation of phosphoric acid by means of carbonate of barium and a ferric salt has already been described (p. 544). Carbonate of barium alone does not precipitate phosphoric acid completely from its aqueous solution; but if the phosphate of any base not precipitated by carbonate of barium, the alkaline earths and magnesia for example, be dissolved in nitric or hydrochloric acid, carbonate of barium will precipitate all the phosphoric acid, together with any of the weaker bases (such as alumina, ferric oxide, or chromic oxide) that may also be present, leaving the stronger bases in solution. This method may be applied to the analysis of mixtures of earthy phosphates, such as occur in soils, coprolites, guano, artificial manures, &c., in which the presence of alumina interferes with the separation by nitric acid and metallic mercury. The phosphate having been dissolved in nitric or hydrochloric acid, and the solution boiled for some time, to convert any pyrophosphoric acid that may be present into orthophosphoric acid, carbonate of barium is to be added, till the free acid is completely saturated, and the liquid left to stand for a few days, with frequent agitation. The washed precipitate, containing alumina and ferric oxide together with phosphate and carbonate of barium, is then to be dissolved in hydrochloric

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acid, and the barium precipitated by sulphuric acid. The filtrate may be treated with citric acid, ammonia, and sulphate of magnesium, to precipitate the phosphoric acid, and the ferric oxide and alumina which remain in solution may be separated by the usual methods. The solution filtered from the precipitate formed by the carbonate of barium is free from phosphoric acid, but contains the nitrates or chlorides of calcium, magnesium, and the alkali-metals, together with nitrate or chloride of barium. It is freed from barium by sulphuric acid; the neutralised filtrate is then treated with oxalic acid to precipitate the calcium; and the magnesium and alkali-metals are separated by the methods described under MAGNESIUM (iii. 753).

When calcium is present in considerable quantity, the washing of the last-mentioned precipitate of sulphate of barium is very tedious and difficult, on account of the sparing solubility of the sulphate of calcium with which it is mixed. In this case it is best, after washing out the more soluble sulphates with water, to treat the remaining precipitate with a solution of carbonate of ammonium, whereby the remaining sulphate of calcium is converted into carbonate; then, after washing, dissolve out the carbonate of calcium with hydrochloric acid, and add the solution to that containing the other bases. (H. Rose, *Traité de Chimie Analytique*, ii. 719.)

*Special Methods of Separation.*—From metals whose sulphides are insoluble in acids (copper, lead, mercury, &c.) phosphoric acid is easily separated by passing sulphydric acid gas through an acid solution of the salt. The phosphoric acid may then be precipitated from the filtrate as ammonio-magnesian phosphate.

Phosphate of zinc dissolved in acetic acid may also be decomposed by sulphydric acid.

The phosphates of iron, magnesium, nickel, cobalt, and uranium are decomposed by sulphide of ammonium, the metals being separated as sulphides; but this mode of separation is not found to give exact results, excepting in the case of iron. A better method is to fuse the phosphates with an alkaline carbonate (p. 546). In the case of uranium, however, the separation by this method is not complete, a certain quantity of uranic oxide always passing into solution together with alkaline phosphate and carbonate. To obtain complete separation, the salt must be fused with about three times its weight of a mixture of carbonate of sodium and cyanide of potassium; the uranium is then wholly separated as protoxide. The fused mass is digested with water containing sal-ammoniac (if pure water is used, the uranous oxide separates in a very finely-divided state, and runs through the filter); the phosphoric acid is precipitated from the filtrate as ammonio-magnesian phosphate; and the insoluble uranous oxide, which retains a small portion of alkali, is dissolved in nitric acid, precipitated by ammonia, washed with water containing a little sal-ammoniac, ignited in a stream of hydrogen, and weighed.

A similar method serves for the separation of phosphoric acid from the oxides of chromium. The chromic oxide, which remains undissolved after the alkaline phosphates, &c. have been washed out, likewise retains a small quantity of alkaline salt, to free it from which, it must be fused with nitre and sodic carbonate, and the resulting chromic acid precipitated by mercurous nitrate, or reduced to chromic oxide by any of the methods described under CHROMIUM (i. 944).

From yttria, thorina, and the oxides of cerium, lanthanum, and didymium, phosphoric acid is easily separated by adding oxalic acid or oxalate of ammonium to the nearly neutralised solution of the phosphate in nitric, hydrochloric, or sulphuric acid. The metal is then completely separated as oxalate, and the phosphoric acid may be precipitated from the filtrate as ammonio-magnesian phosphate. The treatment with nitric acid and metallic mercury may also be applied to the separation of phosphoric acid from these bases, as well as from glucina and zirconia.

From alumina, phosphoric acid is most easily separated by means of citric acid, ammonia, and a magnesium-salt, as already described (p. 547). An older mode of separation, proposed by Berzelius, is to ignite the aluminic phosphate with 2½ pts. of finely-divided silica and 6 pts. of sodic carbonate. The ignited mass (which does not fuse) is digested with water, which dissolves sodic phosphate and carbonate, and a small quantity of sodic silicate, leaving the alumina and the greater part of the silica undissolved; the filtered solution is mixed with excess of hydrochloric acid, and evaporated finally over the water-bath, to render the silica completely insoluble; the residue is boiled with water; and the phosphoric acid precipitated from the filtered liquid as ammonio-magnesian phosphate. The insoluble residue containing the alumina is treated with hydrochloric acid and evaporated to dryness; the residue is moistened with hydrochloric acid, boiled up with water, and filtered to separate the silica; and the alumina is precipitated from the solution by ammonia or carbonate of ammonium. A modification of this method, proposed by Fuchs, consists in dissolving the aluminic phosphate in caustic potash, adding silicate of potassium (soluble glass) and boiling, whereby all the alumina is precipitated as silicate of aluminium and potassium, while

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phosphate of potassium remains in solution. From this solution the phosphoric acid is precipitated as ammonio-magnesian phosphate, and the precipitated silicate is treated as above for the determination of the alumina.

From baryta, phosphoric acid is most easily separated by treating the solution of the compound in hydrochloric acid with sulphuric acid, which precipitates the baryta; from strontia in like manner, with addition of alcohol.

From lime, phosphoric acid is easily separated by precipitating the base as oxalate from the solution of the phosphate in acetic acid, or in hydrochloric or nitric acid mixed with acetate of sodium or ammonium; from magnesia by fusion with an alkaline carbonate, &c. (p. 546), phosphate of magnesium being completely decomposed by this treatment.

When lime and magnesia occur together as phosphates, as in bone-earth and plant-ashes, the substance may be dissolved in hydrochloric acid; the lime precipitated by oxalate of ammonium as above; and the filtrate treated with excess of ammonia, which throws down a precipitate of ammonio-magnesian phosphate, leaving a solution still containing phosphoric acid or magnesia, according as one or the other is in excess. In the former case the phosphoric acid is precipitated by addition of a magnesium-salt; in the latter, the magnesia is precipitated by addition of a soluble phosphate.

Such mixtures or compounds may also be analysed by treatment with nitric acid and metallic mercury, but not by precipitation with solution of mercurous nitrate (p. 546), because a certain quantity of calcic phosphate is always precipitated at the same time. Fusion with an alkaline carbonate is not applicable to them, because phosphate of calcium is but very imperfectly decomposed thereby.

From the alkalis, phosphoric acid may be separated by precipitation with acetate of lead. The precipitated phosphate of lead must be weighed when dry, the quantity of lead contained in it determined, and thence the quantity of phosphoric acid may be calculated. The solution containing the alkalis and the excess of lead-salt is treated with carbonate of ammonium to precipitate the lead; the filtrate is then acidulated with sulphuric or hydrochloric acid; and the alkalis are estimated as sulphates or chlorides.

The separation is, however, more easily effected by means of nitric acid and metallic mercury, especially in the case of the lithium-phosphates, which are but slightly soluble in water. The same method is also the best adapted for analysing the insoluble compounds which the alkaline phosphates form with those of calcium and magnesium. If alumina is also present, it is best, as already observed, to adopt the method of separation by means of carbonate of barium (p. 547). The method of separation by ceric salts might also be applicable to such mixtures (p. 545).

When all the phosphoric acid in an alkaline phosphate is in the state of orthophosphoric acid, it may be completely separated by the easier mode of precipitation with a solution of mercurous nitrate.

### *Separation of Phosphoric Acid from other Acids.*

From sulphuric acid, phosphoric acid is easily separated by precipitating the former as sulphate of barium from an acid solution; if, however, metaphosphoric acid is present, it must first be converted into pyro- or orthophosphoric acid, otherwise the separation will not be complete.

From selenious acid, phosphoric acid is separated by precipitating the selenium with sulphurous acid; the phosphoric acid may then be precipitated from the filtrate as ammonio-magnesian phosphate. If selenic acid is present, it must first be reduced to selenious acid by means of hydrochloric acid. Precipitation with barium-salts does not effect complete precipitation. (See SELENIUM.)

The same method serves for the separation of phosphoric acid from the acids of tellurium.

From hydrochloric, hydrobromic, and hydriodic acids, phosphoric acid is easily separated by precipitating the former acids with nitrate of silver in acid solution. The phosphoric acid may be precipitated from the filtrate as triargentic phosphate, by careful neutralisation with an alkali; or, better, the excess of silver may be removed from the solution by hydrochloric acid, and the phosphoric acid then precipitated as ammonio-magnesian phosphate.

Respecting the separation of phosphoric from hydrofluoric acid, see FLUORINE (ii. 676).

From boric acid, phosphoric acid may be separated in several ways:—*a*. The phosphoric acid may first be thrown down as ammonio-magnesian phosphate, and the boric acid then determined in the filtrate by the methods specially adapted to it (i. 630).—*β*. The solution of a phosphate and a borate in hydrochloric or nitric acid is treated with carbonate of barium, whereby the phosphoric acid is precipitated as phosphate of

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barium, while the whole of the boric acid remains in solution. This mode of separation is not, however, quite exact, as phosphate of barium is not completely insoluble in a liquid containing boric acid.—γ. When the two acids exist in solution in combination with alkalis alone, they may be separated by addition of acetate of potassium, which throws down the whole of the boric acid as hydrofluoborate of potassium (i. 633), leaving the phosphoric acid in solution.

From silicates.—If the silicate is easily decomposible by acids, the whole of the phosphoric acid will be found in the acid liquid obtained by treating it with an acid, and filtering from the silica. If the silicate is free from alumina, it may be decomposed by nitric acid, the resulting liquid evaporated to dryness over a water-bath, the silica separated in the usual manner, and the phosphoric acid separated from the bases in the filtrate by means of nitric acid and metallic mercury.

In silicates of aluminium containing no other base, phosphoric acid may be separated by fusing the compound with an alkaline carbonate, and treating the product in the manner already described (p. 548), the weight of the silica being of course likewise determined. If the substance to be analysed contains large quantities of phosphoric acid and alumina in proportion to the silica, it will be necessary to add a quantity of finely-divided silica, in the proportion of about 1½ pt. silica to 2 pts. of the aluminic phosphate. The weight of this quantity of silica must then be deducted from the total weight of that substance obtained in the analysis. But when, as is more generally the case, the silicate contains other bases, and especially lime, it must be decomposed by an acid, best with hydrochloric acid, the silica separated, and its quantity determined in the usual way (see p. 548, also SILICON); and the phosphoric acid and bases in the filtrate separated by carbonate of barium in the manner already described (p. 547).

Silicates undecomposible by acids must be fused with an alkaline carbonate, the silica separated by hydrochloric acid, and the filtrate treated as above, according to the bases present. If alkalis are present, they must be determined by a special analysis, the silicate being decomposed by hydrofluoric acid. (H. Rose, *Traité de Chimie Analytique*, ii. 896.)

For the methods of determining phosphoric acid and fluorine when they occur together in silicates, see SILICATES.

From titanic acid.—Phosphoric acid forms with titanic acid an insoluble compound, which may be decomposed by fusion with an alkaline carbonate. On treating the fused mass with water, an alkaline titanate remains undissolved, while the alkaline phosphate dissolves.

From molybdic acid, phosphoric acid is separated by sulphide of ammonium, the molybdenum being dissolved thereby as trisulphide, which may be precipitated by an acid. In the filtrate, the phosphoric acid is precipitated as ammonia-magnesian phosphate.

From vanadic acid, phosphoric acid is separated by solution of sal-ammoniac, in which vanadate of ammonium is insoluble. The precipitate is first washed with water containing sal-ammoniac, then with alcohol, and transformed into vanadic anhydride by careful heating. The phosphoric acid is precipitated from the filtrate as ammonio-magnesian phosphate.

### *Metallic Phosphates.*

**Phosphates of Aluminium.** α. *Metaphosphate*, $Al^2O^3.3P^2O^5$ and $Al'''P^3O^9$.—Prepared by dissolving hydrate of aluminium in excess of aqueous phosphoric acid, evaporating, and heating the residue to 316°. It is a white anhydrous salt, insoluble in water and in concentrated acids. (Maddrell, Chem. Soc. Mem. iii. 373.)

β. *Orthophosphates.*—Hydrated orthophosphates of aluminium occur in many minerals often associated with other salts. Gibbsite, kalaite, peganite, fischerite, and wavellite are hydrated phosphates of aluminium, the last-mentioned sometimes also containing fluoride of aluminium; amblygonite is a phosphate of aluminium, lithium, and sodium; lazulite is hydrated phosphate of aluminium associated with ferrous and magnesic phosphates.

Orthophosphates of aluminium are produced by precipitating solutions of aluminium-salts with alkaline phosphates; but the products thus obtained vary considerably in composition, according to the proportions of the acting solutions, the temperature at which they are mixed, and the extent to which the precipitate is washed; the precipitates also frequently retain portions of the soluble aluminium-salt or of the alkaline phosphate.

*Acid salt?*—According to Ludwig, the precipitate formed by phosphate of sodium in a solution of alum, contains, in the anhydrous state, $8Al^2O^3.9P^2O^5$. A solution of aluminic phosphate in aqueous phosphoric acid leaves on evaporation a gummy mass, which melts to a colourless glass.

*Neutral salt*, $Al^2O^3.P^2O^5.6H^2O$, or $Al'''PO^4.3H^2O$ (or with 4 at. or $4\frac{1}{2}$ at. $H^2O$).—Produced by completely precipitating a neutral solution of alum with excess of sodic orthophosphate, best by gradually adding the alum-solution to the soluble phosphate: also when a solution of aluminic phosphate in hydrochloric acid is neutralised with ammonia, or precipitated with acetate of sodium; or when an alkaline solution of aluminic phosphate is neutralised with acetic acid. It is a white bulky precipitate, forming when dry a loose white powder, the amount of water in which appears to vary from 3 to $4\frac{1}{2}$ atoms. *Gibbsite*, from Richmond, Massachussetts, contains, according to Hermann's analysis (J. pr. Chem. xl. 32, xlii. 1), 37·62 per cent. phosphoric anhydride, 26·66 alumina, and 35·72 water, agreeing nearly with the formula $Al^2O^3.P^2O^5.4H^2O$, which requires 36·53 per cent. $P^2O^5$, 26·42 $Al^2O^3$, and 37·05 water. In other samples, however, Hermann found less phosphoric anhydride and more alumina, probably arising from admixture of hydrargyllite (hydrate of aluminium, ii. 838).

*Basic salts.*—*a.* A salt containing $16Al^2O^3.15P^2O^5$, or $Al^2O^3.30Al'''PO^4$, is formed, according to Ludwig, by precipitating a solution of aluminic phosphate in caustic soda-ley with acetic acid, but it is most probably nothing but the neutral salt mixed with free alumina.

*b.* $4Al^2O^3.3P^2O^5.18H^2O$, or $6Al'''PO^4.2Al'''H^3O^3.15aq$.—This is said by Rammelsberg to be the composition of the bulky precipitate formed by adding ammonia to a neutral solution of chloride of aluminium. It is more gelatinous and translucent than the precipitated normal phosphate; retains 15 at. water at 100°. Its composition appears, however, to vary according to the quantity of ammonia added, and the time during which it is left in contact with the precipitate; and, if digested with excess of ammonia for about 24 hours, it gives up part of its acid, and is converted into a hydrate of the salt $2Al^2O^3.P^2O^5$.

*c.* $3Al^2O^3.2P^2O^5.12H^2O$, or $4Al'''PO^4.2Al'''H^3O^3.9aq$.—This is the composition of *Wavellite*, a mineral occurring in trimetric crystals exhibiting the combination $\infty P . \infty \breve{P} \infty . \breve{P} \infty$. Ratio of macrodiaognal, brachydiaognal, and principal axis = 1·4943 : 1 : 0·7431. Angle $\infty P : \infty P = 126·25$. Cleavage rather perfect, parallel to $\infty P$, also parallel to the brachydiagonal. More frequently, however, the mineral forms hemispherical or globular concretions, having a radiate structure. Hardness = 3·25. Specific gravity = 2·337 to 2·3616. Lustre vitreous, inclining to pearly and resinous. Colour white, passing into yellow, green, grey, brown, and black. Streak white. Translucent. Index of refraction = 1·52.—When heated it gives off water, and sometimes also hydrofluoric acid; colours the blowpipe flame a faint bluish-green; swells up on charcoal, turns white, and exhibits the reactions of alumina.

*Analyses.* 1. From Zbirow in Bohemia (Hermann, J. pr. Chem. xxxiii. 288).—2. From Barnstaple in Devonshire (Berzelius, Schw. J. xviii. 288; xxiv. 121).—3. From Steamboat, Chester County, Pennsylvania (Genth, Sill. Am. J. [2] xxiii. 423).—4. From Hungary: *Kapnicite*, specific gravity = 2·356 (Städeler, Ann. Ch. Pharm. cix. 305).

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Fluorine | 1·69 | 2·06 | trace | |
| Phosphoric anhydride | 34·29 | 33·40 | 34·68 | 35·49 |
| Alumina | 36·39 | 35·35 | 36·67 | 39·59 |
| Ferric oxide | 1·20 | 1·25 | 0·22 | |
| Water | 26·34 | 26.80 | 28·29 | 24·92 |
| Lime | | 0·50 | | |
| | 99·91 | 99·36 | 99·86 | 100·00 |

The formula $3Al^2O^3.2P^2O^5.12H^2O$ requires 35·14 per cent. $P^2O^5$, 38·13 $Al^2O^3$, and 26·73 water. Städeler supposes the mineral to contain only 11 at. water.

Berzelius and Hermann regard wavellite as a definite compound of phosphate and fluoride of aluminium; but the quantity of fluorine is so very variable, many specimens containing only traces of it, and some none at all, that its presence is probably only accidental. As the specimen from Barnstaple analysed by Berzelius contained lime, it was probably mixed with fluorspar.

Wavellite occurs also at Amburg in Bavaria, at Langenstriegis near Freiberg, and other localities in Germany; also at Clonmel and Cork in Ireland; in the Shaint islands of Scotland; at Washington Mine, Davidson County, North Carolina; and at Villa Rica, Minas Geraes, in Brazil.

*d.* $2Al^2O^3.P^2O^5$, or $2Al'''PO^4.Al^2O^3$.—This compound appears to be produced, as already stated, by the prolonged action of ammonia on the salt *b*, and occurs in combination with 5, 6, or 8 at. water in the minerals turquois or kalaite, peganite, and fischerite.

*Turquois* or *Kalaite*, $2Al^2O^3.P^2O^5.5H^2O$ or $Al'''PO^4.Al'''H^3O^3$, aq., also called *agaphite* and *johnite*, the *Birousa* of the Persians, and (probably) the *callais* of Pliny, is reniform, stalactitic, or incrusting, with no cleavage; hardness = 6; specific gravity 2·6 – 2·683. It has a somewhat waxy lustre, dull internally; a peculiar bluish-green colour, and white streak; is feebly subtranslucent or opaque, and has a small conchoidal fracture. When heated it decrepitates strongly, giving off water and turning black. Before the blowpipe it does not swell, but becomes brown and vitreous, and colours the inner flame green. With fluxes it gives the reactions of iron and copper. It is soluble in acids, and, according to Hermann, dissolves in water after fusion with potash—the several varieties, however, all leaving more or less insoluble residue. An analysis by Hermann of a blue oriental turquois gave 28·90 per cent. phosphoric anhydride, 47·45 alumina, 2·02 cupric oxide, 1·10 ferric oxide, 0·50 manganic oxide, 1·85 lime, and 18·18 water, whence the mineral appears to consist essentially of $2Al^2O^3.P^2O^5.5H^2O$ mixed with phosphates of calcium, copper, &c. A green oriental turquois (specific gravity 2·621) was found by Hermann to contain only 5·64 per cent. $P^2O^5$, and was evidently a mechanical mixture containing but little real turquois. Turquois occurs in a mountainous district in Persia, not far from Nichabour; a less pure variety is found at Jordansmühle in Silesia, and at Oelsnitz in Saxony. It receives a good polish, and when finely coloured is highly valued as a gem. The *occidental* or *bone turquois* is said to consist of fossil bones or teeth coloured with oxide of copper. (Dana, ii. 405.)

*Peganite*, $2Al^2O^3.P^2O^5.6H^2O$ or $2(Al'''PO^4.Al'''H^3O^3)$, is a green or white mineral occurring at Striegis in Saxony, in small rhombic prisms of 127°, with the acute lateral edges truncated; hardness = 3—4: specific gravity = 2·49—2·54. Contains, according to Hermann (J. pr. Chem. xxxiii. 287), 30·49 per cent. phosphoric anhydride, 44·49 alumina, and 22·82 water.

*Fischerite*, $2Al^2O^3.P^2O^5.8H^2O$ or $2(Al'''PO^4.Al'''H^3O^3).5aq.$, occurs at Nischne Tagilsk, in colourless rhombic prisms of 118° 32′, or dull green masses of specific gravity 2·46; behaves like turquois before the blowpipe, but is not readily dissolved by any acid except sulphuric acid. Gives by analysis 29·03 phosphoric anhydride, 38·47 alumina, and 27·50 water, together with 1·20 ferric and manganic oxides, 0·80 cupric oxide, and 3·00 cupric phosphate and gangue. (Hermann, *loc. cit.*)

All the phosphates of aluminium bear considerable resemblance to alumina, both in the hydrated and in the anhydrous state. The precipitated phosphates are gelatinous masses, which dissolve easily in acids and in caustic fixed alkalis, and are precipitated from their acid solutions by ammonia, carbonate of ammonium, or sulphide of ammonium, and from the alkaline solutions by chloride of ammonium, in their original state, without loss of phosphoric acid. Hence the distinction between hydrate and phosphate of aluminium, and the separation of phosphoric acid from alumina, present considerable difficulties. The methods of detecting and separating the phosphoric acid have been already described, viz.: Precipitation by a magnesium-salt from a solution of the aluminic phosphate in citric acid containing ammonia and chloride of ammonium; precipitation by mercurous nitrate from a solution in nitric acid neutralised by potash; precipitation by molybdate of ammonium, uranic salts, or ceric salts, from slightly acid or neutral solutions; ignition with silica and carbonate of sodium (pp. 545—549).

γ. *Pyrophosphate of Aluminium*, $2Al^2O^3.3P^2O^5.10H^2O = \overset{\text{xii}}{Al}{}^4P^6O^{21}.10H^2O$ (dried at 110°).—Produced by precipitating an aqueous solution of sublimed chloride of aluminium with pyrophosphate of sodium, $4AlCl^3 + 3Na^4P^2O^7 = Al^4P^6O^{21} + 12NaCl$. It is a white amorphous precipitate exactly resembling hydrate of aluminium, insoluble in water and in acetic acid, soluble in other acids, even in sulphurous acid, and separating again from the last-mentioned solution on boiling. It is distinguished from the orthophosphate by being soluble in ammonia as well as in potash; but when its solution in any acid is supersaturated with ammonia, the whole of the aluminium is precipitated as a basic salt no longer soluble in ammonia, while part of the pyrophosphoric acid remains in solution. (Schwarzenberg, Ann. Ch. Pharm. lxv. 2.)

**Phosphates of Ammonium.** α. *Metaphosphates.*—The *monometaphosphate*, $NH^4PO^3$, is formed when the dimetaphosphate is heated for some time to 200°—250°. It is nearly insoluble in water. (Fleitmann.)

The *dimetaphosphate*, $(NH^4)^2P^2O^6$, is produced by the action of sulphide of ammonium containing a little free ammonia on the corresponding copper-salt (p. 539), and separates from the filtrate on addition of alcohol, in monoclinic prisms. It dissolves in 15 pts. water, either cold or hot; may be heated to 300° without loss of ammonia; and when kept for some time between 200° and 250°, becomes opaque without alteration of weight, and is converted into the monometaphosphate. (Fleitmann.)

The *hexmetaphosphate*, $(NH^4)^6P^6O^{18}$ (Graham's salt), is obtained by saturating deliquescent metaphosphoric acid with ammonia and evaporating.

β. The *orthophosphates of ammonium*, $(NH^4)H^2PO^4$, $(NH^4)^2HPO^4$, and

$(NH^4)^3PO^4$, have been already described under AMMONIACAL SALTS (i. 193). The specific gravity of the first is 1·758 (Schiff, Jahresb. 1859, p. 16), of the second 1·678 (Buignet, *ibid.* 1861, p. 15). An orthophosphate of ammonium and aluminium occurs as a white earth in a volcanic grotto in the Isle of Bourbon.

γ. *Pyrophosphates.*—The *neutral salt*, $(NH^4)^4P^2O^7$, separates on adding alcohol to the aqueous acid supersaturated with ammonia, in small acicular laminæ adhering to the sides of the vessel. It is easily soluble in water, forming an alkaline solution which gives off ammonia when heated, and forms acid pyrophosphate of ammonium, but no orthophosphate; the latter is produced, on the other hand, by boiling the solution with excess of ammonia.

The *acid pyrophosphate*, $(NH^4)^2H^2P^2O^7$, is obtained in crystals by adding alcohol to a solution of the neutral salt mixed with alcohol. Its solution is not altered by boiling. (Schwarzenberg.)

**Phosphates of Barium.** α. *Metaphosphates.*—Maddrell's *monometaphosphate of barium* is obtained by evaporating a solution of barytic carbonate in excess of metaphosphoric acid, and heating the residue to 316°, as a white powder which is not altered by the action of dilute acids, but is decomposed by warm concentrated sulphuric acid. It is not decomposed by digestion with an alkaline carbonate, and therefore the particular modification of metaphosphoric acid which it contains cannot be determined with certainty (p. 539).

The *dimetaphosphate*, $Ba''P^2O^6.2H^2O$ (air-dried), separates in crystals on adding chloride of barium to a solution of the corresponding sodium- or ammonium salt. It is very slightly soluble in water, is not decomposed by boiling with hydrochloric or nitric acid, but readily by strong sulphuric acid; when digested with aqueous carbonate of sodium, it is converted into dimetaphosphate of sodium. It does not give off its water at 150°, but at a red heat it becomes anhydrous without melting, and then no longer contains dimetaphosphoric acid, but becomes insoluble in water, and is not decomposed by carbonate of sodium.

The *trimetaphosphate*, $Ba^3P^6O^{18}.6H^2O$, is produced on mixing a solution of 1 pt. of the corresponding sodium-salt in 10 to 15 pts. water, with a nearly saturated solution of 2 or 3 pts. chloride of barium. On leaving the liquid (filtered, if necessary) to itself for a while, the salt separates in beautiful monoclinic prisms, which give off two-thirds of their water at 100°, and the remainder, with intumescence, at a higher temperature. At a red heat it becomes insoluble in acids, but does not fuse. The unignited salt is somewhat more soluble in water than the dimetaphosphate, and when digested with carbonate of sodium yields trimetaphosphate of sodium.

The *hexmetaphosphate* is obtained by precipitating the corresponding sodium-salt (Graham's vitreous sodium-metaphosphate) with chloride of barium, as a gelatinous precipitate becoming translucent and brittle when dry. It is insoluble in pure water, and in water containing sal-ammoniac, easily soluble in nitric acid. When heated, it gives off water without complete fusion, and is afterwards but sparingly soluble in nitric acid. It is decomposed by prolonged boiling with water, being converted into an acid metaphosphate, which gradually dissolves.

β. *Orthophosphates.*—1. The *monobarytic salt*, $Ba''H^4P^2O^8$, prepared by evaporating a solution of the di- or tri-barytic salt in aqueous phosphoric acid, is white, crystalline, apparently triclinic according to Erlenmeyer, permanent in the air and has a slightly sour taste. It dissolves without alteration in dilute acids, but is decomposed by water into free phosphoric acid and the neutral salt.

2. The *dibarytic salt*, $\overset{''}{Ba}{}^2H^2P^2O^8$, is obtained by double decomposition as a scaly, crystalline precipitate, soluble in 20,570 pts. of water at 20°, somewhat more soluble in water containing chloride of barium, chloride of sodium, or ammoniacal salts; according to Ludwig, it dissolves in 4362 pts. water containing 1·2 per cent. chloride of sodium or 0·8 per cent. chloride of barium; addition of pure ammonia renders it less soluble. It dissolves easily in dilute nitric or hydrochloric acid, less easily in acetic acid, of which it requires 400 pts. of specific gravity 1·032 to dissolve it. From the solution in nitric or hydrochloric acid, ammonia added in excess throws down the tribarytic salt (Berzelius) or a salt intermediate between the di- and tri-barytic salts. The precipitates also contain chloride or nitrate of barium, and a small quantity of ammoniacal salt, while neutral phosphate of ammonium remains in the wash-water. (Ludwig, Wackenroder.)

A salt having the composition $\overset{''}{Ba}{}^3H^6P^4O^{16}.3H^2O = Ba''H^4P^2O^8.Ba^2H^2P^2O^8.3H^2O$, intermediate between the mono- and dibarytic orthophosphates, is formed by precipitating a solution of the dibarytic salt with alcohol.

A solution of dibarytic phosphate in nitric acid yields, on addition of ammonia, a

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precipitate consisting of barytic *phosphato-nitrate*, $2\overset{''}{\mathrm{Ba}}{}^2\mathrm{H}^2\mathrm{P}^2\mathrm{O}^8.\mathrm{Ba}''\mathrm{N}^2\mathrm{O}^6$, which, when ignited, leaves a mixture of di- and tri-barytic phosphates. (Wackenroder.)

3. The *tribarytic salt*, $\overset{''}{\mathrm{Ba}}{}^3\mathrm{P}^2\mathrm{O}^8.\mathrm{H}^2\mathrm{O}$, is formed by precipitating chloride of barium with trisodic phosphate, or with disodic phosphate mixed with ammonia, and separates as a heavy granular powder, the supernatant liquid remaining neutral. It gives off water, but not the whole, at 200°, and does not absorb carbonic acid from the air.

A solution of this salt in aqueous phosphoric acid evaporated on the water-bath, deposits a crystalline powder, and if it be then heated to boiling and filtered, the filtrate on further evaporation yields the monobarytic salt in (apparently triclinic) crystals; but if the original solution be at once heated to boiling, it deposits crystalline granules of the dibarytic salt, $\mathrm{Ba}^2\mathrm{H}^2\mathrm{P}^2\mathrm{O}^8$, while the mother-liquor retains a barytic phosphate containing 1 at. barium to 5 at. phosphorus. (Erlenmeyer, Jahresb. 1857, p. 145.)

A saturated solution of tribarytic phosphate in hydrochloric acid, if evaporated and left to cool, deposits crystals of chloride of barium, the mother-liquor, after repeated crystallisation, containing a larger and larger proportion of monobarytic phosphate; and if, after all the chlorine has been separated as chloride of barium, more hydrochloric acid be added, in quantity at least half as great as that originally present, the whole of the barium may be separated as chloride and pure phosphoric acid obtained. If the solution of tribarytic phosphate in hydrochloric acid be evaporated at the boiling heat, shining needles form in the liquid, and, if separated by decantation, immediately crumble to a crystalline powder. A solution from which these crystals had separated, yielded, when mixed with a quantity of water sufficient to redissolve them completely, and, exposed for several months to a summer heat in a vessel covered with filter-paper, hard well-defined crystals of a *phosphato-chloride*, $4(\mathrm{Ba}''\mathrm{H}^4\mathrm{P}^2\mathrm{O}^8).\mathrm{Ba}''\mathrm{Cl}^2$. (Erlenmeyer, Jahresb. 1857, p. 147.)

A salt intermediate between the di- and tri-barytic phosphates, and containing $\overset{''}{\mathrm{Ba}}{}^3\mathrm{P}^2\mathrm{O}^8.\overset{''}{\mathrm{Ba}}{}^2\mathrm{H}^2\mathrm{P}^2\mathrm{O}^8$ or $\overset{''}{\mathrm{Ba}}{}^5\mathrm{H}^2\mathrm{P}^4\mathrm{O}^{16}$ is formed on mixing a solution of the dibarytic salt in hydrochloric acid with a quantity of ammonia exactly sufficient to precipitate it. (Berzelius.) According to Ludwig, a solution of dibarytic phosphate in hydrochloric acid yields on addition of ammonia a *phosphato-chloride of barium* containing $3\overset{''}{\mathrm{Ba}}{}^5\mathrm{P}^4\mathrm{O}^{16}.\mathrm{Ba}''\mathrm{Cl}^2.3\mathrm{H}^2\mathrm{O}$.

γ. *Pyrophosphate*, $\overset{''}{\mathrm{Ba}}{}^2\mathrm{P}^2\mathrm{O}^7$.—Pyrophosphoric acid precipitates baryta-water, but not barium-salts; these salts, however, form with pyrophosphate of sodium, a white, amorphous, pulverulent precipitate of barytic pyrophosphate containing 1 at. water at 100° according to Schwarzenberg, 2 at. according to Gerhardt. It is sparingly soluble in water, aqueous pyrophosphoric acid, and aqueous sulphurous acid; more soluble in hydrochloric or nitric acid; not perceptibly soluble in acetic acid, in water containing-sal-ammoniac, or in excess of sodic pyrophosphate, of which, however, it takes up a certain quantity.

**Phosphates of Bismuth.** α. *Metaphosphate.*—Trioxide of bismuth fused with excess of phosphoric anhydride, forms a clear glass, which on slow cooling with frequent stirring, yields a crystalline salt, apparently consisting of tetrametaphosphate of bismuth. It is insoluble in water, and is decomposed by sulphide of sodium, forming a tenacious mass probably containing tetrametaphosphate of sodium.

A solution of bismuth-nitrate mixed with metaphosphoric acid and then with ammonia forms a precipitate insoluble in excess of ammonia. (Persoz.)

β. *Orthophosphates*, $\mathrm{Bi}'''\mathrm{PO}^4$.—Precipitated by nitrate of bismuth from a solution of orthophosphoric acid containing nitric acid, but free from hydrochloric or sulphuric acid (Chancel, Compt. rend. l. 416; Jahresb. 1860, p. 622). The same salt containing $\frac{3}{2}$ at. water is formed, according to Kühn, by digesting crystallised bismuth-nitrate with ordinary phosphate of sodium.

γ. *Pyrophosphate.*—$2\overset{'''}{\mathrm{Bi}}{}^2\mathrm{O}^3.3\mathrm{P}^2\mathrm{O}^5$ or $\overset{'''}{\mathrm{Bi}}{}^4\mathrm{P}^6\mathrm{O}^{21}$. Obtained by precipitation in the same manner as the orthophosphate. (Chancel.)

**Phosphates of Cadmium.** α. *Metaphosphates.*—When oxide of cadmium is fused with phosphoric anhydride, an insoluble salt separates, which when decomposed by sulphide of alkali-metal yields a *tetrametaphosphate* (Fleitmann). Nitrate of cadmium mixed with metaphosphoric acid and then with ammonia, forms a precipitate which dissolves in excess of ammonia, but separates again as the ammonia evaporates. (Persoz.)

β. *Orthophosphate*, $\overset{''}{\mathrm{Cd}}{}^3\mathrm{P}^2\mathrm{O}^8$.—Obtained by precipitating a neutral solution of a cadmic salt with disodic orthophosphate, as a white insoluble powder, which melts to a transparent glass. According to Kühn, the precipitate sometimes consists of a mixture of di- and tri-cadmic salts.

*Pyrophosphate*, $Cd^2P^2O^7.2H^2O$ (at 100°).—This salt is obtained by precipitation as a white amorphous heavy powder, which dissolves in sulphurous acid and separates in nacreous laminæ on boiling the solution. It is insoluble in water and in potash, soluble in acids, in ammonia, and in excess of sodic pyrophosphate, whence it is precipitated by sulphide of ammonium. When ignited in hydrogen, it gives off a little phosphorous anhydride and phosphoretted hydrogen, yields a small sublimate of cadmium, and leaves a white saline mass still containing phosphoric acid and oxide of cadmium. (Schwarzenberg.)

**Phosphates of Calcium.** α. *Metaphosphates.*—The *monometaphosphate*, $Ca''P^2O^6$, is obtained by dissolving carbonate of calcium in orthophosphoric acid, then evaporating and heating the residue to 316°, as an insoluble white powder, which is not altered by water or dilute acids, but is decomposed by strong sulphuric acid (Maddrell). It is not decomposed by alkaline-carbonates, so that its acid cannot be transferred to other bases. (Fleitmann.)

*Dimetaphosphate of Calcium*, $\overset{''}{Ca}{}^2P^4O^{12}.4H^2O$, is obtained pure and crystalline by precipitating the corresponding potassium- or sodium-salt with excess of chloride of calcium. It is insoluble in water, and is but slightly attacked by strong hydrochloric or nitric acid; but strong sulphuric acid decomposes it completely when heated with it. It gives off all its water at a red heat; the ignited salt no longer contains dimetaphosphoric acid, and is not decomposed by digestion with alkaline carbonates. (Fleitmann.)

*Dimetaphosphate of Calcium and Ammonium*, $Ca''(NH^4)^2P^4O^{12}.2H^2O$, is obtained in spicular crystals by mixing a solution of calcic chloride with excess of the ammonium-salt and adding alcohol. It is insoluble in water, reacts with acids like the pure calcium-salt, and does not give off all its water till heated to redness. The precipitate formed by chloride of calcium and dimetaphosphate of ammonium always contains ammonia, even when the chloride of calcium is added in excess. (Fleitmann.)

β. *Orthophosphates of Calcium.*—1. The *monocalcic salt*, $Ca''H^4P^2O^8$, is produced by dissolving the di- or tri-calcic salt in aqueous phosphoric, nitric, or hydrochloric acid, and crystallises on evaporation in small laminæ or scales containing 1 at. water. It has a strong acid reaction, becomes moist and greasy when exposed to the air, and dissolves readily in water, forming a solution from which alcohol precipitates a mixture of mono- and di-calcic orthophosphates, or a salt of intermediate composition containing $Ca^4H^{10}P^6O^{24} = 2CaH^4P^2O^8.Ca^2H^2P^2O^8$ (Berzelius) or $Ca^3H^6P^4O^{16} = CaH^4P^2O^8.Ca^2H^2P^2O^8$ (Raewsky). According to Erlenmeyer (Jahresb. 1857, p. 145), the crystals of monocalcic phosphate are decomposed by cold water into dicalcic orthophosphate which separates, and a hyperacid salt which remains in solution.

Monocalcic phosphate melts when heated, giving off all its water, and leaving an insoluble metaphosphate. When ignited with charcoal, it gives off carbonic anhydride and phosphorus, and leaves a residue of tricalcic phosphate (p. 500).

Compounds of monocalcic phosphate with chloride of calcium are obtained by evaporating a solution of tricalcic phosphate in hydrochloric acid (p. 557).

An impure mixture of monocalcic phosphate and gypsum, sometimes mixed with organic matter, is much used as a manure, under the name of "superphosphate of lime" or "disintegrated bone-ash;" it is prepared by mixing the ground bones either raw or burnt with 5 to 10 per cent. sulphuric acid. (See Richardson and Watts' *Chemical Technology*, i. [4] 262.)

2. *Dicalcic orthophosphate* or *neutral phosphate of calcium*, $\overset{''}{Ca}{}^2H^2P^2O^8$, is formed by precipitating chloride of calcium with an alkaline orthophosphate, especially when the solutions are slightly acid. The precipitates thus formed vary in their amount of water, and are crystalline or amorphous, and more or less soluble in acids, according to the manner of the precipitation; they often also contain admixed tricalcic phosphate.

*a. Tetrahydrated*, $Ca^2H^2P^2O^8.4H^2O$.—A salt having this composition is the principal constituent of certain ovoïd concretions found in the softened ureters and the cloaca of the sturgeon (called *Belugensteine* in German, from *Bjäluga*, the Russian name of the fish). It is formed when a solution of an alkaline orthophosphate is poured into a solution of chloride of calcium (Raewsky), and may be obtained crystallised by precipitating chloride of calcium with excess of disodic orthophosphate, dissolving the precipitate in acetic acid, and leaving the solution to itself, or by pouring the solution of calcic chloride into a solution of sodic phosphate mixed with a large quantity of acetic acid; or, according to Percy, by completely precipitating chloride of calcium with a very dilute solution of sodic phosphate, and passing carbonic acid into the liquid, whereby a portion of the precipitate is dissolved; the filtered liquid left to itself in a loosely covered vessel deposits the salt in rhombic plates. When a solution of chloride of calcium is precipitated by a slight excess of ordinary sodic phosphate—the solution with the precipitate divided into two equal parts—to one portion just enough nitric or hydrochloric acid added to effect solution without the aid of heat—the other portion then added—and the whole allowed to stand quietly for 48 hours—the amorphous precipitate of dicalcic phosphate increases rapidly in density, and is gradually converted into fine white scales, which, under the microscope, present the appearance of thin tabular rhombic prisms, with the acute prismatic edges generally truncated, so that the crystals have the appearance of irregular six-sided tables. The salt thus formed has the composition above given: it is decomposed by boiling in water, and becomes bulky, opaque, and indistinctly crystalline; the supernatant liquid strongly reddens litmus (Bödeker, Ann. Ch. Pharm. lxix. 206). The same hydrated salt is likewise obtained in rhombic tablets by allowing a solution of disodic phosphate to diffuse slowly into chloride of calcium. (Drevermann.)

Tetrahydrated dicalcic orthophosphate does not lose weight in vacuo at ordinary temperatures, but when heated to 150° it gives off all its water, according to Bödeker; according to Percy, it gives off 2 at. water at 140°.

*b. Trihydrated*, $Ca^2H^2P^2O^8.3H^2O$.—This hydrate separates in right rhombic crystals when limestone is subjected to the action of phosphate of ammonium and carbonic acid (Becquerel), and is obtained as a crystalline precipitate when a solution of sodic phosphate is dropped into a large excess of calcic chloride (Berzelius); also, according to Raewsky, when the solution of calcic chloride is added to the sodic phosphate. It gives off all its water at a red heat.

Dicalcic orthophosphate is nearly insoluble in cold water, and is resolved by boiling with water into insoluble tricalcic and soluble monocalcic phosphate. The precipitated salt dissolves to a slight extent in excess of chloride of calcium, but is reprecipitated on addition of ammonia. It is somewhat more soluble in water containing a small quantity of chloride of sodium, ammoniacal salts, starch, or gelatin, than in pure water. It dissolves readily in nitric and hydrochloric acids; acetic acid likewise dissolves it, but with some difficulty when it is dense, or when it has been precipitated by excess of sodic phosphate; the solution thus obtained, when left to itself, soon deposits the salt in crystals; if, on the contrary, the chloride of calcium was in excess, the salt dissolves more easily in acetic acid, and the solution remains perfectly clear. The salt dissolves also in other organic acids and in carbonic acid. The acid solutions react with alkalis just like solutions of the tricalcic salt. Sulphuric acid decomposes it completely.

3. *Tricalcic orthophosphate* or *Neutral phosphate of calcium*, $\overset{''}{Ca}P^2O^8$ or $3Ca''O.P^2O^5$.—This salt occurs combined with chloride and fluoride of calcium in apatite (i. 348), and pure in osteolite (iv. 247). It forms the chief constituent of the inorganic part of bones, (i. 622); at all events, the precipitate formed by dissolving bone-ash in nitric acid and precipitating with excess of ammonia has this composition; the bones of many animals during life, perhaps, contain somewhat less lime. Bone-ash contains about four-fifths of its weight of tricalcic phosphate, the remainder consisting of phosphate of magnesium and carbonate of calcium; tricalcic phosphate likewise occurs in considerable quantity in the excrements of carnivorous animals and in coprolites. Berzelius formerly supposed that the phosphate of calcium contained in bone-earth was not pure tricalcic phosphate, but that the ignited compound consisted of $8CaO.P^2O^5$ or $2Ca^3P^2O^8.Ca''P^2O^7$.

Tricalcic phosphate is obtained in the amorphous state by precipitating chloride of calcium with trisodic phosphate; by slowly adding a solution of disodic orthophosphate mixed with ammonia to a solution of chloride of calcium, the latter being kept in excess; by mixing chloride of calcium with less than the equivalent quantity of disodic orthophosphate, and precipitating with ammonia; or by treating dicalcic orthophosphate with caustic potash or soda, which abstracts one-third of the acid:

$$3\overset{''}{Ca}H^2P^2O^8 + 2KHO = 2\overset{''}{Ca}{}^3P^2O^8 + 2KH^2PO^4 + 2H^2O.$$

The salt obtained by either of these processes is a translucent gelatinous precipitate which dries up to a white earthy powder.

The salt is obtained in the crystalline state by heating dicalcic pyrophosphate with water, whereby it is resolved into phosphoric acid and tricalcic phosphate, which then separates in rectangular plates:

$$3\overset{''}{Ca}{}^2P^2O^7 + 3H^2O = 2\overset{''}{Ca}{}^3P^2O^8 + 2H^3PO^4.$$

Dicalcic orthophosphate, heated with water to 280°, undergoes a similar but slower and less complete transformation, and the resulting tricalcic salt forms indistinct prisms. (Reynoso.)

The precipitated salt contains in the air-dried state 3 to 6 at. water, 2 at. of which gradually escape at common temperatures; the salt dried at 100° still retains 1 at. water (Ludwig); according to Berzelius, the compound contains 2 at. water; after drying at 200° it is anhydrous. It is not decomposed by simple ignition, but when heated to redness with silica and charcoal, it gives off carbonic oxide and phosphorus (p. 500), and is converted into silicate of calcium.

Tricalcic phosphate is insoluble in pure water, alcohol, and ether, slightly soluble in water containing chloride of sodium, ammoniacal salts, gelatin, starch, and other organic matters; more soluble in water containing carbonic acid. A litre of water saturated with carbonic acid dissolves 0·663 grm. bone-earth, the greater part of which (0·500 grm.) separates on boiling. (Liebig.)

Tricalcic phosphate dissolves easily in nitric and hydrochloric acids, somewhat less easily in acetic acid and other organic acids. It is completely decomposed by excess of sulphuric acid, if not too dilute. A solution of potassic or sodic carbonate does not decompose it in the cold, but partial decomposition takes place on boiling or fusing the salt with an alkaline carbonate. Tricalcic phosphate dissolved in hydrochloric acid is decomposed by ferric, uranic, ceric salts, &c., in the manner already described (pp. 544, 545). From a solution of the salt in nitric acid mixed with acetate of potassium or sodium, acetate of lead throws down all the phosphoric acid as phosphate of lead. From a similar solution the calcium is completely precipitated as oxalate by addition of oxalate of ammonium, the whole of the phosphoric acid remaining in solution.

The salt $8Ca''O.3P^2O^5.H^2O = 2\overset{''}{Ca}{}^3P^2O^8.\overset{''}{Ca}{}^2H^2P^2O^8$, formerly supposed by Berzelius to exist in bone-earth, is generally obtained as a gelatinous precipitate when an acid solution of tricalcic phosphate is treated with ammonia not in excess.

*Phosphato-chlorides of Calcium.*—Some varieties of apatite consist of $3\overset{''}{Ca}{}^3P^2O^8.Ca''Cl^2$; in others the chlorine is wholly or partly replaced by fluorine. A compound of tricalcic phosphate with chloride of calcium is produced artificially by mixing the recently precipitated dicalcic orthophosphate with chloride of calcium, and gradually heating the mixture to redness. Hydrochloric acid then escapes, and the residue still contains chloride of calcium, only a small portion of which can be dissolved out by water. The exact composition of the residue has not been ascertained.

Compounds of monocalcic orthophosphate with calcic chloride are obtained by evaporating a solution of the tricalcic salt in hydrochloric acid. A solution saturated and left to evaporate at common temperatures deposits crusts made up of rhomboidal plates of the salt $7Ca''H^4P^2O^8.Ca''Cl^2.14H^2O$. The same solution evaporated over the water-bath first deposits the dicalcic salt $\overset{''}{Ca}{}^2H^2P^2O^8$, and the filtrate, when further evaporated, yields first a small quantity of the phosphato-chloride just mentioned, then, while the liquid is still warm, white scales having the composition $Ca''H^4P^2O^8.Ca''Cl^2.H^2O$. The same salt is obtained by adding chloride of calcium to a solution of lime in phosphoric acid containing 2 at. CaO to 3 at. $P^2O^5$, and evaporating. At temperatures below 6°, this salt separates partly as above, partly in long needles containing 8 at. water of crystallisation; these, when kept in a closed vessel, are resolved at ordinary temperatures into water and the preceding hydrate. A cold saturated solution of dicalcic phosphate in hydrochloric acid yields, according to the extent to which the evaporation is carried, various mixtures of salts, among which monocalcic orthophosphate appears to occur, but never pure. When a solution of dicalcic orthophosphate in hydrochloric acid is saturated at ordinary temperatures with tricalcic phosphate, then mixed with half the quantity of hydrochloric acid already contained in it, and evaporated at a very gentle heat, so far that it begins to crystallise on cooling below 6°, the crystals thus obtained are very much like the first-mentioned phosphato-chloride; but have the composition $4Ca''H^4P^2O^8.Ca''Cl^2.8H^2O$ and the liquid separated therefrom yields, on further evaporation, the salt $Ca''H^4P^2O^8.Ca''Cl^2$, with 1 or 8 at. water, according to the temperature at which the crystallisation takes place. (Erlenmeyer, Jahresb. 1857, p. 146.)

*Tricalcic phosphate with Aluminic Hydrate*, $\overset{''}{Ca}{}^3P^2O^8.2Al'''H^3O^3$.—A mineral having this composition has lately been found occurring as a light, soft, white powder in cavities and fissures of a mass of quartz-crystals, mixed with iron and copper pyrites and partly coated with childrenite, from Tavistock in Devonshire. Under the microscope it is seen to consist of minute acicular cystals, transparent to translucent and fragile. When heated alone it glows and becomes opaque, and after ignition gives a distinct blue colour with nitrate of cobalt. It gives no colour to a borax bead (unless childrenite is present). It gave by analysis 30·36 per cent. $P^2O^5$, 36·27 $Ca''O$, 22·40 $Al^2O^3$, and 12·00 water; the above formula, or $3Ca''O.P^2O^5.\overset{vi}{Al}{}^2O^3 + 3H^2O$, requiring 30·41 $P^2O^5$, 35·97 $Ca''O$, 22·06 $Al^2O^3$, and 11·56 water. (Church, Chem. Soc. J. xviii. 263.)

A mineral, supposed to be a hydrated calcio-aluminic phosphate, was found by Damour (Instit. 1853, p. 77; Jahresb. 1853, p. 930) in the diamond sand of Bahia. It occurred in rounded pebbles containing 12·7 per cent. water.

γ. *Pyrophosphate of Calcium*, $\overset{\prime\prime}{Ca}{}^2P^2O^7$.—Aqueous pyrophosphoric acid precipitates lime-water, but not calcium-salts. Chloride of calcium yields with pyrophosphate of sodium a white amorphous precipitate of calcic pyrophosphate; and if this precipitate is dissolved in a saturated aqueous solution of sulphurous acid, and the solution heated, the salt separates, as the sulphurous acid escapes, in the form of a crystalline crust, which floats on the surface of the liquid at first, but ultimately sinks at the bottom. It is soluble to a small extent in water, insoluble in acetic acid and solution of sodic pyrophosphate (Schwarzenberg). Like dicalcic orthophosphate, it is more or less soluble in acetic acid, according as it has been precipitated from a solution containing excess of chloride of calcium or of the alkaline pyrophosphate (Baer). It is easily soluble in nitric and hydrochloric acid, nearly insoluble in aqueous pyrophosphate of sodium. The crystalline salt contains 4 at. water, 1½ at. of which are retained at 100° and 1 at. at 110°. (Schwarzenberg.)

**Phosphates of Cerium.** The only known phosphate of cerium is the tricerous orthophosphate, $Ce^3P^2O^8$, which occurs as a natural mineral both in the anhydrous and the hydrated state, and is formed artificially by precipitating a cerous salt with phosphoric acid or a soluble phosphate. The precipitate is white, pulverulent when dry, insoluble in water and in aqueous phosphoric acid, slightly soluble in hydrochloric and nitric acids. When strongly ignited in a charcoal-lined crucible, it is neither fused or reduced, but merely cakes together.

Anhydrous tricerous phosphate occurs in *Cryptolite* and *Phosphocerite*, associated in the latter, and probably also in the former, with the corresponding phosphates of lanthanum and didymium; also, together with phosphate of lanthanum (and probably also of didymium), phosphate of thorinum, and a small quantity of phosphate of calcium, in *Monazite*.

*Cryptolite* was discovered by Wöhler in the rose-coloured apatite of Arendal in Norway, from which it is separated by dissolving the apatite in nitric acid. The cryptolite is then left undissolved, together with microscopic crystals of magnetic iron-ore, hornblende, and an unknown substance of a hyacinth-red colour, likewise containing cerium. The crystals of cryptolite are hexagonal prisms about a line in length, and of a wine-yellow colour. By exposure to a moderate heat, they undergo no change either in appearance or in weight. Specific gravity = 4·6. Decomposed by strong sulphuric acid, the whole being reduced to a dry earthy mass.

*Phosphocerite* was discovered by Mr. Ollive Sims in the cobalt-ore of Johannisberg in Sweden, of which it forms about the one-thousandth part. It remains when the ore after calcination is treated with hydrochloric acid for the purpose of extracting the cobalt, as a greyish-yellow crystalline powder, associated with a small quantity of minute dark purple crystals, which are strongly attracted by the magnet, and appear to consist of magnetic iron-ore and oxide of cobalt. The crystals of phosphocerite, when examined by the microscope, present two forms—one an octahedron (not regular), the other a four-sided prism with quadrilateral summits; both forms appear to belong to the trimetric system. Hardness, between 5·0 and 5·5 (Chapman, Chem. Soc. Qu. J. ii. 154). Specific gravity = 4·78 (Watts). When exposed to the blowpipe flame it vitrefies partially on the edges and surface, tinging the flame at the same time slightly green. With the usual blowpipe reagents, it presents the reactions of cerium, imparting however to the borax and phosphate of soda glasses, when cold, a pale violet-blue tint, either owing to the presence of didymium or to the admixture of a small portion of the cobalt-ore. With borax and soft iron wire it produces a brittle phosphide of iron (Chapman). Oil of vitriol aided by gentle heat decomposes it, forming a pasty mass, which is soluble in cold water, with the exception of a small quantity of silica.

*Analyses: a. Cryptolite* (Wöhler, Ann. Ch. Pharm. lvii. 268).—*b. Phosphocerite* (Watts, Chem. Soc. Qu. J. ii. 181).

| | *a.* | *b.* |
|---|---|---|
| Phosphoric anhydride . . . | 27·37 | 29·33 |
| Protoxide of cerium, &c. . . . | 70·26 | 66·65 |
| Protoxide of iron . . . . | 1·51 | 2·70 $Fe^3O^4$ |
| Protoxide of cobalt . . . . | . . | 0·46 |
| | 99·14 | 99·14 |

Both these analyses agree approximately with the formula $\overset{\prime\prime}{Ce}{}^3P^2O^8$ or $3CeO.P^2O^5$, which requires 36·47 per cent. $P^2O^5$ and 69·53 CeO. A closer agreement is scarcely to be expected, inasmuch as the oxides of lanthanum and didymium, which exist in large quantity in phosphocerite, and are probably also present in cryptolite, were not separated from the cerous oxide. Phosphocerite is especially remarkable for the large amount of didymium contained in it. If this is also the case with cryptolite, there can be but little doubt of the identity of the two minerals, for the differences observed in the crystalline forms cannot be regarded as important, or as quite distinctly made out, inasmuch as the crystals are merely microscopic.

Hydrated tricerous phosphate has lately been found by Church (Chem. Soc. J. xviii. 259) in a crystallised mineral from Cornwall, occurring as a thin crust of very minute crystals, closely investing a quartzose matrix. The crystals are generally arranged in fan-like groups of single rows of prisms, having their faces of union parallel to the larger lateral prismatic planes. Sometimes the structure is almost columnar, or in radiating groups, presenting a drusy surface, and in general appearance somewhat like that of wavellite. The crystals appear to be monoclinic, and are prismatically developed. The end-face oP is usually an unmodified rhomboid; sometimes, however, its acute angles are truncated. Cleavage parallel to oP, very perfect; the crystals are cleavable also, parallel to a plane replacing the acute solid angles or acute prismatic edges; also parallel to the larger lateral prismatic planes. The crystals are fragile, transparent to translucent, with vitreous lustre, bright, pearly on the end-faces; colour pale smoke-grey inclining to flesh-red; streak and powder white. The crystals are doubly refractive. Hardness rather above 3; specific gravity approximately = 3·14. The mineral heated alone in a tube becomes opaque, and gives off water, having a very faint acid reaction. In the outer blowpipe-flame it becomes reddish, and then exhibits the difficult solubility of cryptolite. It melts and dissolves completely in borax, forming in the oxidising flame a bead, which is opaline and orange-yellow while hot, colourless or slightly amethystine when cold.

The mineral gives by analyses (mean) 14·93 per cent. phosphoric anhydride, 51·87 cerous oxide, 5·42 lime, and 14·93 water, agreeing nearly with the formula $5Ce''O.Ca''O.2P^2O^5 + 8H^2O$ or $(\frac{5}{6}Ce''.\frac{1}{6}Ca'')^3P^2O^8.4H^2O$, which requires 27·73 per cent. $P^2O^5$, 52·73 $Ce''O$, 5·47 $Ca''O$, and 14·07 water. (Church, Chem. Soc. J. xviii. 259.)

**Phosphates of Chromium.**—α. *Chromic metaphosphate*, $Cr^2O^3.3P^2O^5$, or $Cr'''P^3O^9$, is obtained as a green anhydrous salt, perfectly insoluble in water and in acids, by evaporating a solution of chromic oxide in excess of aqueous orthophosphoric acid, and heating the residue to 316°. (Maddrell.)

β. *Chromous orthophosphate* is a blue precipitate, formed on adding ordinary phosphate of sodium to the solution of chromous chloride. It is easily soluble in acids, and turns green on exposure to the air. (Moberg.)

γ. *Chromic orthophosphate*, $Cr'''PO^4$.—A solution of chromic chloride made as neutral as possible forms with phosphate of sodium a green precipitate, which turns blue-black in drying. (Vauquelin; see also Dowling and Plunkett, Chem. Gaz. 1858, 220.)

When disodic orthophosphate is added by drops to a solution of chrome-alum, but not in sufficient quantity to throw down all the chromium, a bulky precipitate is formed consisting of $Cr'''PO^4.6H^2O$, which, on standing, becomes dark violet and crystalline. The filtrate from this precipitate, if treated with a quantity of sodic phosphate sufficient to precipitate nearly all the chromium, yields a pentahydrated salt, $Cr'''PO^4.5H^2O$, less crystalline and somewhat lighter in colour than the preceding. If the solution of chrome-alum be added by drops to the solution of sodic phosphate, a flocculent green precipitate is formed, consisting of a trihydrate, $Cr'''PO^4.3H^2O$. (Rammelsberg.)

δ. *Chromic pyrophosphate*, $2Cr^2O^3.3P^2O^5 = \overset{\prime\prime\prime}{Cr}{}^4P^6O^{21}$.—Formed by precipitating a solution of crystallised chrome-alum with sodic pyrophosphate. At ordinary temperatures, a dirty red precipitate appears, but with a boiling solution a pale green precipitate is obtained. This salt is soluble in solution of sodic pyrophosphate; in strong mineral acids; in water acidulated with sulphuric acid, from which it is again precipitated in an amorphous state on boiling; and in solution of potash. At 100° it assumes a deeper green colour, but after ignition appears paler. The hydrate contains 7 atoms of water. (Schwarzenberg.)

**Phosphates of Cobalt.** α. *Metaphosphates.*—The *monometaphosphate*, $Co''P^2O^6$, separates as a rose-red powder when sulphate of cobalt is heated with excess of orthophosphoric acid to 316°. It is insoluble in water and in dilute acids, decomposed by warm sulphuric acid, scarcely acted upon by sulphide of ammonium. (Maddrell.)

The *hexmetaphosphate* is obtained by precipitating chloride of cobalt (not the sulphate) with the corresponding sodium-salt. The precipitate is red, and is converted by agitation into oily drops soluble in excess of the sodium-salt. (H. Rose.)

*β. Orthophosphate.* $\overset{''}{Co}{}^3P^2O^8.8H^2O$.—Obtained by treating a cobalt-salt with disodic orthophosphate, as a reddish-blue flocculent precipitate, which dissolves in excess of the cobalt-salt, forming a red solution, which yields on boiling a red precipitate, redissolving as the liquid cools. By decomposing pyrophosphate of cobalt with water at 180°, the same salt is obtained in small rose-coloured crystals, which, when heated, give off water and turn reddish-blue. By heating carbonate of cobalt with excess of phosphoric acid to 150°—160° in a sealed tube, a hydrated salt, $Co^2P^4O^8.2H^2O$, is obtained in crystals. (Debray, Ann. Ch. Pharm. cxv. 50.)

Orthophosphate of cobalt is insoluble in water, and but very slightly soluble even in presence of ammoniacal salts, but dissolves in acids and in free ammonia. By igniting in hydrogen gas it is reduced to tricobaltic phosphide, $Co^3P^2$. The precipitated salt is used as a pigment. (Salvétat, Compt. rend. xlviii. 295.)

A mixture of cobalt-phosphate and alumina yields when ignited a fine blue colour, known as *Leyden* (more properly *Leithner's*) or *Thénard's blue*, or *cobalt-ultramarine*. It is prepared by mixing 16 pts. of recently precipitated gelatinous alumina with 2 pts. phosphate (or 1 pt. arsenate) of cobalt, drying the mixture thoroughly, and then gradually heating it to redness. (Handw. d. Chem. vi. 362.)

*γ. Pyrophosphate of Cobalt* obtained by precipitation is soluble in excess of the alkaline pyrophosphate and in ammonia. (Schwarzenberg.)

**Phosphates of Copper.** *α. Metaphosphate.*—This salt is obtained by mixing cupric sulphate, nitrate or oxide with a slight excess of aqueous phosphoric acid (best in the proportion of 4 at. cupric oxide to 5 at. phosphoric anhydride), evaporating and heating the mass with constant stirring to 350°, till it no longer spirts, and phosphoric acid begins to escape in white vapours. The mass when cold is to be washed with cold water till the wash-water no longer exhibits any acid reaction; the cupric metaphosphate then remains in a pulverulent, indistinctly crystalline, anhydrous salt. If a larger excess of phosphoric acid is used, and the mixture very strongly heated over a lamp, and then left to cool very slowly, the cupric metaphosphate separates in shining crystals, which are larger and more distinct in proportion as the mass has been more slowly cooled.

Anhydrous cupric metaphosphate is bluish-white; quite insoluble in water, nearly insoluble in most acids and alkalis, even when concentrated, but dissolves easily in ammonia. It is easily decomposed by sulphide of ammonium or potassium, less easily by sulphide of sodium, yielding in each case an alkaline dimetaphosphate: hence the salt is inferred to be cupric dimetaphosphate, $Cu^2P^4O^{12}$ or $2CuO.2P^2O^5$. It is decomposed by warm strong sulphuric acid with formation of orthophosphoric acid.

The same salt is obtained in small well defined hydrated crystals, $Cu^2P^4O^{12}.8H^2O$, by mixing moderately concentrated solutions of cupric chloride and sodic dimetaphosphate; from dilute solutions it easily separates on addition of alcohol. It is light blue, insoluble in water; does not part with its water of crystallisation at 100°. (Fleitmann.)

*Ammonio-cupric metaphosphate*, $Cu''(NH^4)^2P^4O^{12}.4H^2O$, is obtained in confused needle-shaped crystals on mixing moderately concentrated solutions of ammonium-dimetaphosphate and cupric chloride, the former in excess, and adding alcohol. It is bright blue, sparingly soluble in water, gives off a small portion of its water at ordinary temperatures, but still retains 2 at. water at 100°. Sometimes the crystals formed by precipitation as above contain only 2 at. water, and these are permanent in the air; but the circumstances which determine the formation of one hydrate or the other are not exactly understood. (Fleitmann.)

*β. Orthophosphates.*—An *acid orthophosphate* is obtained as a green gummy mass by evaporating a solution of the tricupric salt in aqueous phosphoric acid.

*Dicupric orthophosphate*, $\overset{''}{Cu}{}^2H^2P^2O^8$, is obtained as a blue-green flocculent precipitate by completely precipitating cupric sulphate with disodic orthophosphate. It is insoluble in water, sparingly soluble even in presence of ammoniacal salts, but dissolves easily in acids, even in acetic acid. By ignition with charcoal it is reduced to dicupric phosphide, $Cu^2P^2$.

The *tricupric salt*, $\overset{''}{Cu}{}^3P^2O^8$, is produced by precipitating cupric sulphate with such a quantity of disodic orthophosphate as to leave the former in excess, or by heating cupric pyrophosphate with water to 280°. The first method yields it as a blue-green amorphous precipitate. The second, in dark yellowish-green crystals, but containing 3 at. water. It behaves with water and other reagents like the dicupric salt, and is reduced by ignition with charcoal to tricupric phosphide, $Cu^3P^2$.

Several hydrated basic cupric orthophosphates, or compounds of cupric orthophosphate with cupric hydrate, occur as natural minerals; their formulæ are as follows:

| | | | |
|---|---|---|---|
| Libethenite . . . . | $4\mathrm{Cu''O.P^2O^5.H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.Cu''H^2O^2}$ |
| Pseudolibethenite . . . | $4\mathrm{Cu''O.P^2O^5.2H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.Cu''H^2O^2}$.aq. |
| Tagilite . . . . . | $4\mathrm{Cu''O.P^2O^5.3H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.Cu''H^2O^2}$.2aq. |
| Dihydrite . . . . . | $5\mathrm{Cu''O.P^2O^5.2H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.2Cu''H^2O^2}$ |
| Ehlita . . . . . | $5\mathrm{Cu''O.P^2O^5.3H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.2Cu''H^2O^2}$.aq. (?) |
| Phosphochalcite . . . | $6\mathrm{Cu''O.P^2O^5.3H^2O}$ | = | $\overset{''}{\mathrm{Cu}}{}^3\mathrm{P^2O^8.3Cu''H^2O^2}$ |

**Libethenite** occurs at Libethen in Hungary and at Nischna Tagilsk in the Ural, in trimetric crystals. Ratio of axes, $a : b : c = 0{\cdot}9158 : 1 : 0{\cdot}6749$. Angle $\infty P : \infty P = 84° 58'$; $\breve{P}\infty : \bar{P}\infty$ (basal) $= 68° 2'$. Ordinary combination $\infty P . \breve{P}\infty . P$, the two former faces greatly predominating. It is isomorphous with olivenite, $\overset{''}{\mathrm{Cu}}{}^3\mathrm{(As; P)^2O^8.Cu''H^2O^2}$. Cleavage parallel to $\infty\breve{P}\infty$ and $\infty\bar{P}\infty$ very indistinct. It likewise occurs in globular and reniform compact masses. Hardness = 4. Specific gravity = 3·6—3·8. It is subtransparent or subtranslucent, with olive-green colour and streak, and resinous lustre. Fracture subconchoïdal to uneven. Brittle. When heated it gives off water and blackens. It colours the blowpipe flame faintly blue and after being moistened with hydrochloric acid, distinctly blue, and melts to a blackish mass which solidifies in the crystalline state. It is partially reduced on charcoal, completely on addition of sodic carbonate. The other cupric hydrophosphates exhibit similar characters when heated. They all dissolve in acids with blue or green colour, in ammonia with pure blue colour.

*Analyses of Libethenite.*—*a.* From Libethen; crystallised (**Kühn**, Ann. Ch. Pharm. li. 124).—*b.* The same (**Bargamann**, Pogg. Ann. civ. 190).—*c.* From Nischna Tagilsk; crystallised (**Hermann**, J. pr. Chem. xxxvii. 175):

| | $\mathrm{P^2O^5}$ | $\mathrm{As^2O^5}$ | $\mathrm{Cu''O}$ | $\mathrm{H^2O}$ | | |
|---|---|---|---|---|---|---|
| *a.* | 29·44 | . . | 66·94 | 4·05 | = | 100·43 |
| *b.* | 26·46 | 2·30 | 66·29 | 4·04 | = | 99·09 |
| *c.* | 28·61 | . . | 65·89 | 5·50 | = | 100 |

The formula $4\mathrm{Cu''O.P^2O^5.H^2O}$ requires 29·72 per cent. $\mathrm{P^2O^5}$, 66·51 $\mathrm{Cu''O}$, and 3·77 $\mathrm{H^2O}$.

**Pseudolibethenite** from Libethen (so-called libethenite) analysed by **Berthier**. (Ann Min. viii. 334), contains 28·7 per cent. $\mathrm{P^2O^5}$, 63·9 $\mathrm{Cu''O}$ and 7·4 water; that from Linz on the Rhina (so-called ehlite) blackish green, and of specific gravity 4·27, analysed by **Rhodius** (Ann. Ch. Pharm. lxii. 371), contains 28·9 $\mathrm{P^2O^5}$, 63·1 $\mathrm{Cu''O}$ and 7·3 water. The formula $4\mathrm{Cu''O.P^2O^5.2H^2O}$ requires 28·64 $\mathrm{P^2O^5}$, 64·10 $\mathrm{Cu''O}$ and 7·26 water.

**Tagilite**, a mineral from Nischna Tagilsk, occurring in emerald-green masses of specific gravity 3·5, contains 26·91 per cent. $\mathrm{P^2O^5}$, 62·38 $\mathrm{Cu''O}$ and 10·71 water (**Harmann**, *loc. cit.*); the formula $4\mathrm{Cu''O.P^2O^5.3H^2O}$ requires 27·64 $\mathrm{P^2O^5}$, 61·85 $\mathrm{Cu''O}$ and 10·51 water.

**Dihydrite**, occurring at Virneberg near Rheinbreitenbach, and at Nischna Tagilsk, in small dark green crystals, resembling phosphochalcite in physical characters, contains:

| | $\mathrm{P^2O^5}$ | $\mathrm{Cu''O}$ | $\mathrm{H^2O}$ | | | |
|---|---|---|---|---|---|---|
| Virneberg . . | 24·70 | 68·20 | 5·97 | = | 98·87 | **Arfvedson**; Berz. Jahresb. iv. 143. |
| Nischna Tagilsk . | 25·30 | 68·21 | 6·49 | = | 100 | **Hermann**, *loc. cit.* |

The formula $5\mathrm{Cu''O.P^2O^5.2H^2O}$ requires 24·69 $\mathrm{P^2O^5}$, 69·06 $\mathrm{Cu''O}$, and 6·25 water.

**Ehlite** (which contains vanadium) has been already described (ii. 367). Cupric hydrophosphates are also found at Virnaberg and Nischne Tagilsk containing quantities of water intermediate between those belonging to dihydrite and ehlite. (**Rammelsberg's** *Mineralchemie*, p. 346.)

**Phosphochalcite** forms hemihedral trimetric crystals, resembling monoclinic forms. Ratio of axes, $a : b : c = 0{\cdot}667 : 1 : \sqrt{2}$. Angle $\infty P : \infty P = 109° 28'$; $oP : \bar{P}\infty = 146° 18\tfrac{1}{2}'$. Observed combination $\infty\bar{P}2 . \infty\breve{P}\infty . P . oP . \bar{P}\infty . \breve{P}\infty . \bar{P}2 . \tfrac{1}{2}\bar{P}\infty$. Cleavage parallel to $\infty\breve{P}\infty$, imperfect. It also occurs reniform and massive, indistinctly fibrous, with a drusy surface. Hardness = 4·5 to 5. Specific gravity = 4 to 4·4. Lustre adamantine inclining to vitreous. Colour dark green. Streak a little lighter. Transparent to subtranslucent. Fracture small conchoïdal. Brittle.

*Analyses.*—*a.* From Virnaberg (**Rhodius**, Ann. Ch. Pharm. lxii. 37).—*b.* From Ehl on the Rhina (**Bargemann**, Pogg. Ann. civ. 190).—*c.* From Hirschberg in the Voigtland (**Kühn**, Ann. Ch. Pharm. xxxiv. 218):

| | $P^2O^5$ | $As^2O$ | $Cu''O$ | $H^2O$ | | |
|---|---|---|---|---|---|---|
| *a.* | 20·4 | . . | 70·8 | 8·4 | = | 99·6 |
| *b.* | 19·89 | 1·78 | 69·97 | 8·21 | = | 99·85 |
| *c* | 20·87 | . . | 71·73 | 7·40 | = | 100 |

The formula $6Cu''O.P^2O^5.3H^2O$ requires 21·11 $P^2O^5$, 70·87 $Cu''O$ and 8·02 water.

Thrombolite is an amorphous mineral from Retzbanya, consisting approximately of 41·0 $P^2O^5$, 39·2 $Cu''O$, and 16·8 water, whence it is probably $5Cu''O.3P^2O^5.10H^2O$ or $\overset{''}{Cu}{}^3P^2O^8.2Cu''P^2O^6.10H^2O$. (Plattner, J. pr. Chem. xv. 321.)

γ. *Cupric Pyrophosphate*, $\overset{''}{Cu}{}^2P^2O^7.H^2O$ (at 100°), prepared by precipitating a cupric salt with pyrophosphate of sodium, is an amorphous greenish-white powder, which becomes dark blue when dried at 100°, and assumes a lighter blue colour on ignition. It dissolves in mineral acids and ammonia, and likewise in pyrophosphate of sodium. When boiled with caustic potash, it is resolved into cupric oxide and orthophosphate of potassium. Sulphurous acid dissolves it without converting it into a cuprous salt, and the solution when boiled deposits it again in the crystalline state. It gives off its water on ignition.

An *ammoniacal cupric pyrophosphate* $3\overset{''}{Cu}{}^2P^2O^7.2(N^2H^6Cu'')''O.4H^2O$ or $\left.\begin{matrix}\overset{''}{Cu}{}^8\\ \overset{iv}{(P^2O^3)^3}\\ H^{12}\end{matrix}\right\}\begin{matrix}N^4\\ O^{14}\end{matrix}.4H^2O$ separates gradually from an ammoniacal solution of cupric pyrophosphate covered with a layer of alcohol, in nodular groups of ultramarine-coloured crystals, which must be dried over a mixture of sal-ammoniac and quick-lime, to prevent them from giving off ammonia.

**Phosphate of Didymium,** $\overset{''}{Di}{}^3P^2O^8.2H^2O$, separates slowly from a mixture of the concentrated solutions of nitrate of didymium and disodic orthophosphate, quickly on diluting the liquid or on boiling. It is white, pulverulent, insoluble in water, slightly soluble in dilute, easily in concentrated acids; gives off its water at a heat near redness. (Marignac.)

When a solution of didymic sulphate is mixed with an equivalent quantity of phosphoric acid (1 at. $P^2O^5$ to 3 at. $Di''O$), two-thirds of the didymium is precipitated in the form of a phosphate which in the dry state contains $3Di''O.2P^2O^5.5H^2O$, while the rest remains dissolved and is precipitated by ammonia as a translucent jelly, which dries up to translucent rose-red lumps having a conchoïdal fracture. (Hermann, Jahresb. 1861, p. 176.)

**Phosphates of Glucinum.** A neutral solution of nitrate of glucinum forms with disodic orthophosphate a white, amorphous, pulverulent precipitate, which when dried over chloride of calcium, consists of *diglucinic orthophosphate* $\acute{G}{}^2H^2P^2O^8.6H^2O$. With pyrophosphate of sodium a white pulverulent precipitate of glucinic pyrophosphate $\acute{G}{}^2P^2O^7.5H^2O$ is obtained. (Scheffer, Ann. Ch. Pharm. cix. 144; Jahresb. 1859, p. 140.)

**Phosphates of Iron.**—*a. Ferric Metaphosphate*, $Fe^2O^3.3P^2O^5$ or $Fe'''P^3O^9$. Produced by evaporating a solution of ferric chloride with excess of phosphoric acid, and heating the residue to 316°. The white powder which separates is insoluble in water and in dilute acids; strong sulphuric acid decomposes it. (Maddrell.)

β. *Ferric Orthophosphates.*—The precipitates formed by treating soluble ferric salts with alkaline phosphates, vary greatly in composition according to the nature of the solutions used and the proportions in which they are mixed.

*Normal ferric orthophosphate*, $Fe^2O^3.P^2O^5$ or $Fe'''PO^4$ is formed on adding disodic orthophosphate to a solution of ferric chloride or sulphate, made as neutral as possible, or mixed with a considerable quantity of an alkaline acetate (p. 544). The same salt is gradually produced when a solution of ferrous sulphate is mixed with disodic orthophosphate till a permanent precipitate begins to form, and the filtrate is exposed to the air.

Ferric phosphate thus prepared is a white powder insoluble in water, nearly insoluble in acetic acid, slightly soluble in water containing carbonic acid. It dissolves in dilute mineral acids, and is precipitated therefrom by alkalis and alkaline carbonates, and likewise by alkaline acetates. In presence of excess of sodic phosphate, the precipitate of ferric phosphate is dissolved by ammonia and by carbonate of ammonium. Ferric phosphate is soluble in ferric chloride and slightly also in ferric acetate, but quite insoluble in ferrous acetate. Hence when a solution of ferric phosphate in an acid is mixed with ferric chloride and an alkaline acetate, a small portion of it remains dissolved; but if the ferric salt be first reduced to ferrous salt by sulphurous acid, and then treated with ferric chloride and alkaline acetate, the whole of the phosphoric acid is precipitated as ferric phosphate: the precipitation is much accelerated by boiling.

Ferric phosphate slowly gives up its acid to aqueous alkalis. When an acid solution of the salt is precipitated by ammonia, a brown basic salt is formed containing $3Fe^2O^3.2P^2O^5.16H^2O$ or $Fe^2O^3.4Fe'''PO^4.16H^2O$. By boiling with potash-ley a still larger quantity of acid is removed, and the residue contains 15 at. $Fe^2O^3$ to 1 at. $P^2O^5$ (Rammelsberg), probably a mixture of the normal salt with ferric oxide. To remove the whole of the phosphoric acid, the salt must be fused with an alkali or alkaline carbonate.

Ferric phosphate dissolves also with facility in tartaric acid, citric acid, tartrate of ammonium, citrate of sodium and citrate of ammonium. The last mentioned solution when spread upon glass, dries up to brownish-green scales which dissolve in cold water, forming a solution having an agreeable saline taste; they contain 44 per cent. ferric phosphate, $Fe'''PO^4$, 46 per cent. citrate of ammonium, and 10 per cent. water; this salt may be used in medicine. (Heydenreich, Chem. News, iv. 158.)

Ferric phosphate in acid solution is completely decomposed by addition of ammonia and sulphide of ammonium, the whole of the iron being precipitated as sulphide, and the whole of the phosphoric acid remaining in solution.

The white neutral salt gives off its water at a red heat and turns brown. On charcoal before the blowpipe it is reduced to an ash-grey bead; under fluxes it is reduced only at very high temperatures. When strongly ignited over a lamp in a stream of hydrogen gas, it is reduced to ferrous pyrophosphate, $\overset{''}{Fe}{}^2P^2O^7$, which if further heated to whiteness in the gas, is completely deoxidised and converted into a phosphide of iron, $Fe^4P^3$. (Struve, Jahresb. 1860, p. 76.)

A *basic ferric phosphate* containing $2Fe^2O^3.P^2O^5$ or $Fe^2O^3.2Fe'''PO^4$, occurs in nature combined with various quantities of water.

**Cacoxene**, $2Fe^2O^3.P^2O^5.12H^2O$, from the Hrbeck mine near Zbirow in Bohemia, forms yellow or brownish radiated tufts becoming brown on exposure. Hardness = 3·4. Specific gravity = 3·38. An analysis by v. Hauer (Jahrb. d. geol. Reichsanst. 1854, p. 67), gave 19·63 per cent. $P^2O^5$, 47·64 $Fe^2O^3$, and 32·73 water, the formula requiring 20·94 $P^2O^5$, 47·20 $Fe^2O^3$, and 31·86 water; but different specimens present great diversities of composition, arising from alteration, or the presence of foreign substances.

**Dufrenite** or **Green iron ore**, $2Fe^2O^3.P^2O^5.5H^2O$, has been already described (ii. 347).

**Delvauxene** or **Delvauxite** (ii. 340), is an iron ore of variable composition, some specimens containing $2Fe^2O^3.P^2O^5.18H^2O$, others containing the same with $24H^2O$, while others contain lime, and according to v. Hauer, may be represented by the formula, $\overset{''}{Ca}{}^3P^2O^8.2(Fe^2O^3.Fe'''PO^4).24H^2O$.

**Carphosiderite** (from the mica slate of Labrador) is a hydrated ferric phosphate containing small quantities of manganese and zinc, but it has not been analysed quantitatively. It occurs in straw-yellow reniform masses and incrustations, having a resinous lustre and a greasy feel. Hardness = 4—4·5. Specific gravity = 2·49—2·5. (Dana, ii. 431.)

**Bog iron ore** (iii. 338) also contains variable quantities of phosphoric acid. Many other iron ores also contain small quantities of that acid, in consequence of which, pig iron, especially that prepared by the hot blast, generally contains small quantities of phosphorus. In many strata, ferric phosphate occurs in considerable quantity together with phosphate of calcium. In some of the lower strata of the chalk-formation of Sussex, Herapath found as much as 25 per cent. ferric phosphate, and in many coprolites, from 7 to 9 per cent.

A *hydro-ferric phosphate* or *acid ferric phosphate*, containing $Fe'''H^3P^2O^8.2H^2O$, is said to separate from a solution of the normal salt in aqueous phosphoric acid, left to itself in a closed vessel, in transparent cubic crystals, which are tasteless, insoluble in water, but soluble with brown-yellow colour in ammonia (Winckler).—According to L. Gmelin (*Handbook*, v. 226), the salt, $\overset{'''}{Fe}{}^2H^3P^3O^{12}.6H^2O$ or $\left.\begin{matrix}2Fe^2O^3\\3H^2O\end{matrix}\right\}3P^2O^5.12H^2O$, is precipitated by disodic orthophosphate from a solution of ferric chloride, according to the equation:

$$2FeCl^3 \quad + \quad 3Na^2HPO^4 \quad = \quad \overset{'''}{Fe}{}^2H^3P^3O^{12} \quad + \quad 6NaCl;$$

but according to most authorities the precipitate thus formed consists of normal ferric orthophosphate, $Fe'''PO^4$, and phosphoric acid, $H^3PO^4$, remains in solution (p. 562).

*Ammonio-ferric phosphate.*—Ferric phosphate dissolves in ammonia in presence of phosphate of sodium, forming a red-brown solution which gives off ammonia on evaporation.

*γ. Ferrous Orthophosphate.* $3Fe''O.P^2O^5.8H^2O = \overset{\prime\prime}{Fe}{}^3P^2O^8.8H^2O$.—This salt is formed as a white crystalline mass when a plate of iron is left immersed for a long time in a solution of phosphate of ammonium in an open vessel, or when a solution of disodic orthophosphate is decomposed by a very weak voltaic current with a plate of iron for the positive electrode (Becquerel). It may be prepared by dissolving metallic iron in phosphoric acid, or by boiling ferrous sulphate with disodic orthophosphate, both solutions having been previously de-aerated by boiling. The white precipitate must be protected from the air during washing and drying. If the solution of ferrous sulphate is poured into the phosphate of sodium, the precipitate is said to contain diferrous orthophosphate, $Fe^2H^2P^2O^8$, as well as the triferrous salt.

Triferrous orthophosphate is white, insoluble in pure water, slightly soluble in water containing carbonic acid (in 1,000 pts. of water containing rather more than its own volume of carbonic anhydride: Pierre). It dissolves easily in dilute mineral acids and in 560 pts. water containing $\frac{1}{580}$th of commercial acetic acid: also in ammonia, forming a yellowish solution which soon becomes turbid by oxidation on exposure to the air; and in 1,666 pts. water containing 150 pts. of a concentrated solution of acetate of ammonium. The precipitated phosphate dissolves in excess of the soluble ferrous salt. It melts before the blowpipe and solidifies to a crystalline mass on cooling; when fused with sodic carbonate on charcoal, it is reduced to phosphide of iron.

When precipitated ferrous phosphate is washed with water containing air and dried in contact with the air, it is converted by oxidation into a lavender-blue *ferroso-ferric phosphate* containing, according to Rammelsberg, $2\overset{\prime\prime}{Fe}{}^3P^2O^8.(\overset{\prime\prime\prime}{Fe}{}^2O^3.2Fe'''PO^4).16H^2O$.

Triferrous phosphate occurs native as vivienite or blue iron earth, more frequently, however, altered by oxidation to ferroso-ferric phosphate. This mineral forms monoclinic crystals in which the orthodiagonal, clinodiagonal, and principal axis are as 1·3843 : 1 : 1·002. Angle of inclined axes = 71° 25′: ∞P : ∞P = 111° 12′ oP : [P∞] = 145° 33′. Dominant combination ∞P∞ . [∞P∞] . ∞P . ∞P3 . + P . − P . + $\frac{1}{2}$P . − $\frac{1}{2}$P. Cleavage parallel to [∞P∞] highly perfect; parallel to ∞P∞ and $\frac{1}{2}$P∞ in traces. It often occurs also reniform and globular, with divergent, fibrous, or earthy structure; also incrusting. Hardness = 1·3—2. Specific gravity = 2·661. Lustre pearly or metallic-pearly on the faces [∞P∞], vitreous on other faces. Colour usually blue to green, deepening on exposure; in perfectly unaltered specimens colourless. Streak bluish-white, soon changing to indigo-blue; dry powder liver-brown. Transparent or translucent, becoming opaque on exposure. Fracture not observable. Thin laminæ flexible. Sectile.

*Analyses.*—*a.* From Delaware; colourless, turning green on exposure (Fisher, Sill. Am. J. [2] ix. 84).—*b, c.* Crystallised, altered by oxidation; *b* from Bodenmais; *c* from Mullica Hill, Gloucester County, New Jersey (Rammelsberg, *Mineralchemie*, p. 326).—*d.* From Allentown, Monmouth County, New Jersey: earthy (Karlbaum, Sill. Am. J. [2] xxiii. 422).—*e.* From Kertsch in the Crimea: light blue (Struve, J. pr. Chem. xx. 236).—*f.* From Bargusin, Lake Baikal: earthy; dirty-blue (Struve, *loc. cit.*).—*g.* From Kertsch: dark brown, crystalline; specific gravity, 2·72 (Struve, *loc. cit.*):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* |
|---|---|---|---|---|---|---|---|
| Phosphoric anhydride | 27·17 | 29·01 | 28·60 | 29·65 | 29·17 | 19·79 | 28·73 |
| Ferric oxide | . . | 11·60 | 11·91 | 18·45 | 21·34 | 33·11 | 38·20 |
| Ferrous oxide | 44·10 | 35·65 | 34·52 | 27·62 | 21·54 | 13·75 | 9·75 |
| Water | 27·95 | . . | 26·13 | 25·60 | 27·50 | 26·10 | 24·12 |
| Magnesia | . . | . . | . . | 0·03 | . . | 7·37 | |
| Silica | 0·10 | | | | | | |
| | 99·32 | . . | 101·16 | 101·35 | 99·55 | 100·12 | 100·80 |

*a* agrees nearly with the formula of hydrated triferrous phosphate, $3FeO.P^2O^5.8H^2O$ or $Fe^3P^2O^8.8H^2O$ (calc. 28·29 $P^2O^5$, 43·03 $Fe^4O$, 28·68 $H^2O$); *b* and *c* with that of a ferroso-ferric phosphate containing $6(3FeO.P^2O^5.8H^2O) + 3(Fe^2O^3.2P^2O^5.8H^2O)$, which requires 29·00 per cent. $P^2O^5$, 12·24 $Fe^2O^3$, 33·06 $FeO$, and 25·70 water. The remaining analyses may be represented approximately by the following formulæ:

*d.* $3FeO.P^2O^5 + Fe^2O^3.P^2O^5 + 12aq.$
*e.* $3(3FeO.P^2O^5) + 4Fe^2O^3.3P^2O^5 + 45aq.$
*f.* $3FeO.P^2O^5 + 2(3Fe^2O^3.2P^2O^5) + 33aq.$
*g.* $2(3M''O.P^2O^5) + 3Fe^2O^3 + 21aq.$

Crystals of vivianite have been found in the hollow of a bone belonging to the skeleton of a miner discovered in an old working at Tarnowitz (Haidinger, J. pr. Chem. xliv. 81). Schlossberger (Ann. Ch. Pharm. lxii. 382) mentions that some iron nails found in the stomach of an ostrich, and partly enveloped in black animal matter, became covered, after several days' exposure to the air, with blue spots, apparently arising from the formation of vivianite.

Ferrous phosphate occurs, with other metallic phosphates, in several minerals. Childrenite (i. 869) is a phosphate of iron, aluminium, and manganese; triplite (p. 571), phosphate of iron and manganese; triphylline (p. 572), a phosphate of iron, manganese, and lithium.

A compound of *diferrous orthophosphate* with *nitrous oxide*, $\overset{\prime\prime}{\mathrm{Fe}}{}^2\mathrm{H}^2\mathrm{P}^2\mathrm{O}^8.\mathrm{NO}$, is obtained as a brown precipitate on adding disodic orthophosphate to a solution of a ferrous salt saturated with nitric oxide. When exposed to the air, it absorbs oxygen and is converted into ferric phosphate and nitrate. (Handw. d. Chem. vi. 354.)

*Ammonio-ferrous orthophosphate*, $(\mathrm{NH}^4)^2\overset{\prime\prime}{\mathrm{Fe}}{}^2\mathrm{P}^2\mathrm{O}^8.2\mathrm{H}^2\mathrm{O}$.—This salt, analogous in composition to ordinary ammonio-magnesian phosphate dried at 100°, is formed by mixing a solution of 14 pts. of iron in hot hydrochloric acid with a small portion of sulphite of ammonium; adding to it while hot a thoroughly boiled aqueous solution of 100 pts. crystallised ordinary phosphate of sodium, which immediately precipitates white ferrous phosphate; then adding ammonia in slight excess—immediately closing the flask, which must be completely filled with the liquid—agitating—and leaving the mixture to itself for a few minutes, till the precipitate, which is flocculent at first, is converted into laminæ, which sink rapidly to the bottom. If it remains flocculent, the liquid must be heated again, perhaps with the addition of a small quantity of ammonia; if part only of the precipitate becomes crystalline, the lighter flakes must be separated by levigation from the crystalline laminæ. The laminæ, on which the air no longer exerts any oxidising action, are then thrown upon a filter, washed with thoroughly boiled water, and dried. No ammonia must be added to the water, because it immediately induces oxidation, so that hydrated ferric oxide remains on the filter, and the water runs off brown; hence also, in preparing the salt, care must be taken not to add too much ammonia. It forms greenish-white, soft laminæ, which when rubbed on the hand, produce a coating like silver; they are permanent in the air; the salt when heated in the air gives off water and ammonia, and leaves first, greenish ferrous phosphate, amounting to 77 per cent.—then yellowish-white ferric phosphate. With potash-solution it evolves ammonia, and when boiled therewith, gives up its phosphoric acid and is converted into ferroso-ferric oxide having the form of the original laminæ. It is insoluble in water, even at the boiling heat. While yet moist it dissolves readily in acids, even when dilute; but after drying, it dissolves but sparingly and with difficulty even in concentrated acids. (Otto, J. pr. Chem. ii. 409.)

δ. ***Ferric Pyrophosphate***, $2\mathrm{Fe}^2\mathrm{O}^3.3\mathrm{P}^2\mathrm{O}^5.9\mathrm{H}^2\mathrm{O} = \overset{\prime\prime\prime}{\mathrm{Fe}}{}^4\mathrm{P}^6\mathrm{O}^{21}.9\mathrm{H}^2\mathrm{O}$.—Obtained by dissolving sublimed ferric chloride in water, and precipitating by phosphate of sodium; the supernatant liquid is neutral. It is a nearly white powder, having a slight yellowish tinge, which deepens at 100°, and becomes lighter again after ignition; dissolves in acids and in phosphate of sodium, likewise in ammonia; in the latter it forms a yellow solution. It is insoluble in hydrochloric acid, sulphurous acid, and sal-ammoniac. On dissolving it in hydrochloric acid without boiling, and precipitating by ammonia, the precipitate dissolves completely in excess of ammonia. Carbonate of ammonium dissolves it, forming a colourless solution, whereas the ordinary phosphate forms a yellow solution. It is completely decomposed by fusion with a mixture of carbonate of sodium and carbonate of potassium. After drying at 100°, it lost by ignition 17·66 per cent. of water, and the ignited salt was found to contain 41·7 $\mathrm{Fe}^2\mathrm{O}^3$ + 58·3 $\mathrm{P}^2\mathrm{O}^5$.

Acid ferric chloride precipitated by pyrophosphate of sodium, yields, not ferric pyrophosphate, but an orthophosphate containing 1 atom of base to 1 atom of acid; in 100 parts: 61·66 $\mathrm{Fe}^2\mathrm{O}^3$ + 48·34 $\mathrm{P}^2\mathrm{O}^5$. This salt, when boiled with ordinary phosphate of sodium, does not yield pyrophosphate of soda, as is the case with the preceding. (Schwarzenberg, Ann. Ch. Pharm. lxv. 153.)

ε. ***Ferrous Pyrophosphate***, $\overset{\prime\prime}{\mathrm{Fe}}{}^2\mathrm{P}^2\mathrm{O}^7$, is produced by strongly igniting normal ferric orthophosphate in a stream of hydrogen. If further heated to whiteness in the same gas, it suffers further reduction, giving off phosphoretted hydrogen, phosphorous acid, and phosphorus, and leaving a greyish-white, metallic-shining, non-magnetic phosphide of iron, having nearly the composition $\mathrm{Fe}^4\mathrm{P}^3$ (Struve, Jahresb. 1860, p. 76). Ferrous pyrophosphate is likewise obtained by treating a ferrous salt with pyrophosphate of sodium, as a white amorphous precipitate, which turns green and brown on posure to the air. (Schwarzenberg.)

**Phosphate of Lanthanum.**—A solution of sulphate of lanthanum mixed with an equivalent quantity of phosphoric acid, yields a precipitate of an acid orthophosphate $3\text{La}''\text{O}.2\text{P}^2\text{O}^5$, or $\overset{''}{\text{La}}{}^3\text{P}^2\text{O}^8.\text{P}^2\text{O}^5$, but when phosphoric acid is gradually added to a warm solution of the lanthanum-salt, a white, pulverulent precipitate is formed, consisting of the normal salt $\overset{''}{\text{La}}{}^3\text{P}^2\text{O}^8$ (R. Hermann, J. pr. Chem. lxxxii. 385). The latter occurs together with phosphate of cerium in monazite, cryptolite, &c. (p. 558).

**Phosphates of Lead.** *a. Metaphosphates.*—1. *Dimetaphosphate*, $\text{Pb}''\text{O}.2\text{P}^2\text{O}^5 = \overset{''}{\text{Pb}}{}^2\text{P}^4\text{O}^{12}$. A solution of sodic dimetaphosphate mixed with excess of lead-nitrate deposits this salt after a while in tolerably distinct crystals; by precipitation with the ammonium-salt, it is obtained at once as an amorphous precipitate. It is anhydrous, nearly insoluble in water, melts without intumescence at a red heat, and solidifies to a transparent glass on cooling. (Fleitmann.)

*Dimetaphosphate of lead and ammonium*, $(\text{NH}^4)^2\text{Pb}''\text{P}^4\text{O}^{12}$, is obtained by treating the lead-salt just described with excess of dimetaphosphate of ammonium, or by precipitating nitrate of lead with excess of the ammonium-salt. It forms crystalline spangles sparingly soluble in water, and but slowly attacked by acids. It does not lose weight at 150°, and gives off ammonia only on prolonged agitation. (Fleitmann.)

2. *Trimetaphosphate*, $3\text{Pb}''\text{O}.3\text{P}^2\text{O}^5.3\text{H}^2\text{O}$ or $\overset{''}{\text{Pb}}{}^3\text{P}^6\text{O}^{18}.3\text{H}^2\text{O}$.—Obtained by mixing a moderately concentrated solution of sodic trimetaphosphate with an equivalent quantity of lead-nitrate; the liquid (to be filtered if turbid), deposits the salt on standing, in small crystals, which are very slightly soluble in water, and give off their water of crystallisation with intumescence when heated. A solution of the sodium-salt precipitated with acetate of lead yields a salt containing excess of base. (Fleitmann and Henneberg.)

3. *Tetrametaphosphate*, $\overset{''}{\text{Pb}}{}^4\text{P}^8\text{O}^{24}$.—When protoxide of lead is heated for some time with excess of phosphoric acid, a salt separates which redissolves quickly and completely in the excess of acid, and if the fused mass is allowed to cool slowly, separates in large transparent prisms enveloped in an amorphous vitreous mass containing oxide of lead. This mass may be removed by prolonged treatment with cold water, the tetrametaphosphate of lead then remaining undissolved. It is insoluble in water, melts when heated, and forms an amorphous vitreous mass on rapid cooling. It is decomposed by sulphide of ammonium and monosulphide of sodium even in the cold, yielding the corresponding salt of the alkali-metal. When heated with dilute acids, it is dissolved and decomposed much more easily than the dimetaphosphate. (Fleitmann.)

4. *Hexmetaphosphate* (?).—Nitrate of lead mixed with metaphosphoric acid and then with ammonia forms a bulky precipitate insoluble in excess of ammonia. Ordinary metaphosphate of sodium forms with acetate of lead a bulky precipitate, which cakes together when agitated, becomes resinous on standing, and dissolves in excess of ammonia. (H. Rose.)

*β. Orthophosphates.*—An *acid* orthophosphate of lead is said to be formed when lead is dissolved in aqueous phosphoric acid out of contact with the air. The solution yields on evaporation granular crystals, which have not been analysed.

*Diplumbic orthophosphate*, $\left.\begin{matrix}2\text{Pb}''\text{O}\\ \text{H}^2\text{O}\end{matrix}\right\}\text{P}^2\text{O}^5 = \overset{''}{\text{Pb}}{}^2\text{H}^2\text{P}^2\text{O}^8$.—Dilute solutions of lead-nitrate yield with alkaline phosphates, precipitates which are mixtures of di- and tri plumbic orthophosphates in varying proportions. To obtain the diplumbic salt pure, a boiling solution of lead-nitrate is precipitated by aqueous phosphoric acid. The precipitate consists of dazzling white microscopic crystalline laminæ; it is insoluble in water and in aqueous phosphoric acid, but soluble in nitric acid and in potash. By digestion with ammonia it is converted into the triplumbic salt. It melts before the blowpipe, forming a clear bead which exhibits crystalline facets on cooling, but not so distinctly as the triplumbic salt when similarly treated.

*Triplumbic phosphate*, $\overset{''}{\text{Pb}}{}^3\text{P}^2\text{O}^8$, is obtained as a white, earthy, amorphous precipitate, by decomposing acetate of lead with disodic orthophosphate, the lead-salt being kept in excess, or by the action of ammonia on the diplumbic salt; and in rhombic tablets by heating the pyrophosphate $\text{Pb}^2\text{P}^2\text{O}^7$ with water in a sealed tube (Reynoso). It is insoluble in water, moderately soluble in dilute nitric acid, nearly insoluble in acetic acid, easily soluble in potash-ley. When suspended in water, it is decomposed by sulphuric or sulphydric acid. It melts on charcoal before the blowpipe, and the bead on cooling exhibits shining crystalline facets.

By precipitating solutions of nitrate or chloride of lead with phosphate of sodium, double salts are often formed consisting of nitrate or chloride of lead, combined with

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di- or tri-plumbic phosphate. The *phosphato-nitrate*, $Pb^3P^2O^8.PbN^2O^6.2H^2O$, is described under NITRATES (p. 95).

*Phosphato-chlorides.*—The salts $Pb^2H^2P^2O^8.PbCl^2$, $2Pb^3P^2O^8.PbCl^2$ and $3Pb^3P^2O^8.PbCl^2$, obtained by precipitating chloride of lead in various ways with disodic orthophosphate, have been already described as *chlorophosphates* of lead (iii. 339).

Pyromorphite or Green lead ore (*Grünbleierz*) has the composition of the last-mentioned salt, $3Pb^3P^2O^8.PbCl^2$, the phosphorus being, however, often more or less replaced by arsenic. This mineral is isomorphous with mimetesite, or arsenato-chloride of lead, $3Pb^3As^2O^8.PbCl^2$ (in which also the arsenic is often partially replaced by phosphorus); also with apatite; and a variety is known, called *brown lead ore*, consisting of pyromorphite combined with fluor-apatite (i. 349).

The crystals of pyromorphite are hexagonal prisms exhibiting the same combinations as mimetesite (iii. 1024). Length of principal axis = 0·7362. Angle P : P (terminal) = 142° 12′; (lateral) = 80° 44′. Hardness = 3·5—4; specific gravity = 6·5871 : 7·048. Lustre resinous. Colour green, yellow and brown of different shades. Streak white, sometimes yellowish. Subtransparent to subtranslucent. Fracture subconchoïdal, uneven. Brittle. Before the blowpipe it melts very easily, and colours the outer flame blue-green; the bead solidifies like that of phosphate of lead above described. Sometimes emits arsenical fumes.

*Analyses.*—*a.* From Zschopau in Saxony: green; specific gravity = 6·27 (Wöhler, Pogg. Ann. iv. 101).—*b.* From Leadhills in Scotland: orange-red (Wöhler, *loc. cit.*).—*c.* From Mechernich in the Eifel (Bergemann, *Rammelsberg's Mineralchemie*, p. 356).—*d.* From Kransberg in Nassau: crystallised; light green; specific gravity = 7·1 (Sandberger, J. pr. Chem. xlvii. 462).—*e.* From Ems in Nassau: yellow; crystallised (Sandberger *loc. cit.*).—*f.* From Beresow in Siberia: crystals accompanied by vanadinite: specific gravity = 6·715 (Struve, Verh. d. min. Ges. zu. Petersb. 1857).—*g.* From Zschopau: white; crystallised (Wöhler, *loc. cit.*)—*h.* From the Altai: yellow spherical masses; specific gravity = 5·537 (Struve, *loc. cit.*).—*i.* From Rosiers near Pontgibaud, Auvergne: green and brownish; botryoidal; specific gravity = 6·57 (Klaproth, *Beiträge*, iii. 146; v. 200):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
|---|---|---|---|---|---|---|---|---|---|
| Chlorine | 2·57 | 2·52 | 2·50 | 2·67 | 2·89 | 2·54 | 2·56 | 2·58 | 2·59 |
| Lead-oxide | 82·25 | 82·46 | 80·21 | 81·62 | 82·20 | 81·34 | 83·55 | 81·53 | 75·80 |
| Phosphoric anhydride | . . | . . | . . | 15·94 | 15·96 | 15·82 | 15·17 | 12·90 | 14·05 |
| Arsenic anhydride | . . | . . | . . | . . | . . | . . | 2·30 | 2·61 | 3·83 |
| Water | . . | . . | 0·70 | . . | . . | 0·59 | | | |

The variety *g* has the composition of an isomorphous mixture of 1 at. mimetesite and 10 at. pyromorphite; *i*, of 1 at. mimetesite and 8 at. pyromorphite.

The following are analyses of Brown lead ore:—*a.* From the Sonnenwirbel mine near Frieberg: Polyspherite: brown spherules and drops: specific gravity = 6·092 (Kersten, Schw. J. lxii. 1).—*b.* From Mies in Bohemia: botryoidal; specific gravity = 6·444 (Kersten).—*c.* From the same locality: crystallised; specific gravity = 6·983 (Kersten).—*d.* From Bleistadt in Bohemia: crystallised; specific gravity = 7·009 (Kersten).—*e.* From the same: specific gravity = 6·843 (Lerch, Ann. Ch. Pharm. xlv. 328).—*f.* From England: crystallised (Kersten):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|
| Chlorine | 2·62 | 2·76 | 2·50 | 2·56 | 2·47 | 2·60 |
| Lead-oxide | 72·17 | 75·83 | 81·33 | 81·46 | 80·38 | 82·08 |
| Lime | 6·47 | 3·71 | 0·43 | 0·32 | 0·81 | 0·32 |
| | | | | | $Fe''O$ 0·38 | |

If all the chlorine be supposed to be combined with lead, and the admixed apatite to be a pure fluor-apatite, these analyses may be included under the formula:

$$n(Pb''Cl^2.3\ddot{P}b^3P^2O^8) + (Ca''F^2.3\overset{\prime\prime}{C}a^3P^2O^8).$$

the value of *n* being 3 in *a*, 6 in *b* and 48 in *c*, so that the last is nearly pure pyromorphite, as are also *d*, *e*, and *f*.

Nussierite, a mineral from the Nussière mine near Beaujeu, Dept. of the Rhone, containing, according to Barruel (J. pr. Chem. x. 10), 7·65 $Pb''Cl^2$, 46·50 $Pb''O$, 12·30 $Ca''O$, 2·44 $Fe''O$, 19·80 $P^2O^5$, 4·06 $As^2O^5$ and 7·20 silica, is probably an impure pyromorphite.

γ. ***Pyrophosphate of Lead***, $\ddot{P}b^2P^2O^7.H^2O$ (at 100°).—Precipitated on adding pyrophosphate of sodium to excess of nitrate of lead, as a bulky white powder, insoluble in water, acetic acid, sulphurous acid, and ammonia; soluble in nitric acid and in potash (Schwarzenberg). If the pyrophosphate of sodium is added in slight excess, the precipitate contains variable quantities of alkali; a larger excess redissolves the precipitate.

**Phosphates of Lithium.** Only the orthophosphates are known.—*Monolithic orthophosphate*, $Li^2H^2PO^4$, is obtained by mixing one of the two following salts with phosphoric acid and evaporating; or by heating acetate of lithium with excess of phosphoric acid, in which case it separates in rather large crystals. It is deliquescent and very soluble in water, forming an acid solution which is immediately precipitated by silver-salts, but not by chloride of barium except on addition of ammonia. It does not give off any water at 100°; but at 200° half the basic water is evolved and the whole at a red heat, the residue then consisting of metaphosphate of lithium.

*Dilithic orthophosphate* has not been obtained pure, but a salt intermediate between this and the trilithic salt, viz. $Li^5HP^2O^8.H^2O$ or $Li^2HPO^4.Li^3PO^4.H^2O$, is formed on precipitating chloride of lithium with orthophosphate of ammonium, as a crystalline powder, which dissolves in 200 pts. of water, and gives off half its water of crystallisation at 100°, the rest at a higher temperature.

*Trilithic phosphate*, $2Li^3PO^4.H^2O$, is produced by precipitating a neutral acetate of lithium with di-ammonic orthophosphate, or the acid acetate with phosphate of ammonium and free ammonia; also by heating carbonate of lithium with not too large a quantity of aqueous phosphoric acid. It is a white crystalline powder, requiring 833 pts. of water at 12° to dissolve it. It gives off its water of crystallisation when heated, but does not fuse at a red heat.

*Lithio-aluminic phosphate*, $Li^6Al'''P^3O^{12}.15H^2O$.—Prepared by precipitating a saturated solution of aluminic phosphate in caustic potash with chloride of lithium. The washed and dried precipitate is a white powder insoluble in water, easily soluble in acids, and giving off a large quantity of water when heated.

Amblygonite (i. 164) is a lithio-aluminic phosphate having the lithium partly replaced by sodium, and containing also fluorides of aluminium, lithium, and sodium. Rammelsberg (*Mineralchemie*, p. 359), represents it by the formula $(5M^2O.3P^2O^5 + 5Al^2O^3.3P^2O^5) + 2(MF.AlF^3)$, where M denotes lithium and sodium.

Triphylline is a phosphate of lithium, aluminium, iron and manganese (see p. 572).

*Lithio-ammonic phosphate*, $Li^2(NH^4)PO^4$, separates on mixing aqueous phosphate of lithium with di-ammonic orthophosphate and slowly evaporating; if a portion of the ammonia has been lost by too rapid heating, free ammonia must be added. The salt is granulo-crystalline, like ordinary ammonio-magnesian phosphate; slightly soluble in water; melts at a somewhat high temperature, giving off water and ammonia, and when heated before the blowpipe is coloured blue, not red, by nitrate of cobalt.

*Lithio-calcic phosphate*, $LiCa''PO^4$.—Obtained, like the analogous double salts, by igniting 1 at. pyrophosphate of calcium with 1 at. carbonate of lithium. It is insoluble in water. (H. Rose.)

**Phosphates of Magnesium.**—*a. Metaphosphates.* 1. The *monometaphosphate*, $Mg''P^2O^6$, is obtained as a white powder by dissolving carbonate of magnesium in aqueous phosphoric acid, evaporating and heating the residue to 316°. It also separates from the solution of impure phosphoric acid obtained from bones, when strongly concentrated. It is insoluble in water and in dilute acids, and is not decomposed by digestion with alkaline carbonates or phosphates. (Maddrell.)

The *dimetaphosphate*, $\overset{\prime\prime}{M}g^2P^4O^{12}.9H^2O$, (or $10H^2O$), separates gradually from a concentrated solution of the corresponding ammonium-salt mixed with chloride of magnesium, in crystalline crusts which adhere to the sides of the vessel; more quickly on addition of alcohol. It is insoluble in water, is decomposed by acids, gives off 1 at. water at 100°, and the whole without fusion at a red heat. The ignited salt is not decomposed by digestion with alkaline carbonates. (Fleitmann.)

*Hexmetaphosphate.*—Ordinary phosphate of sodium forms a precipitate with acetate, but not with sulphate of magnesium, even at boiling heat. The precipitate is soft and tenacious (Graham). A solution of sulphate of magnesium mixed with not too large a quantity of sodic metaphosphate, forms with ammonia a precipitate which dissolves in sal-ammoniac. (H. Rose.)

*Ammonio-magnesic metaphosphate* (?)—When metaphosphoric acid is dissolved in ammonia in a vessel which is kept cool, and sulphate of magnesium is added in such proportions as to leave the ammonium-salt in excess, a precipitate is formed, consisting of feathery flocks which unite on standing into a soapy mass, drying up to a brittle transparent mass. This salt exhibits the characters of a metaphosphate, but contains according to Wach (Schw. J. lix. 297), a larger proportion of base, being represented by the formula $4Mg''O.(NH^4)^2O.4P^2O^5.16H^2O$; so that it is perhaps a mixture of metaphosphate and pyrophosphate.

*β. Orthophosphates.*—*a. Acid salt.* By evaporating a solution of tri-magnesic phosphate in aqueous phosphoric acid, or by boiling the neutral phosphate with water, and evaporating the filtrate, an acid syrup is obtained which is resolved by alcohol into the trimagnesic salt and free phosphoric acid. When a concentrated solution of magnesia in aqueous phosphoric acid is mixed with alcohol, an oily liquid separates which contains 4 at. magnesia to 3 at. phosphoric anhydride, and may be represented by the formula $Mg''HPO^4.Mg''H^4P^2O^8 + xH^2O$. (**Kühn**, Arch. Pharm. [2] lix. 129.)

*Dimagnesic salt*, $\overset{''}{Mg}{}^2H^2P^2O^8.14H^2O$ or $Mg''HPO^4.7H^2O$.—Produced by precipitating sulphate of magnesium with excess of disodic orthophosphate. When 2 pts. sulphate of magnesium dissolved in 32 pts. water are mixed with 3 pts. disodic orthophosphate dissolved in 32 pts. water, the salt separates in the course of 24 hours in tufts of prisms or needles.

The crystallised salt forms small six-sided needles, having a cooling sweetish taste, and sparingly soluble in water; 1 pt. of the salt dissolves after long standing in 322 pts. water; the clear solution becomes turbid when heated, from separation of trimagnesic salt, which partly redissolves on cooling, and on continued boiling a larger quantity of the latter separates, while the liquid acquires an acid reaction. The salt dissolves easily in dilute acids. The crystals effloresce in warm air, give off 8 at. water at 100°, the remaining six at 170°, and the basic hydrogen as water at a red heat, leaving pyrophosphate of magnesium.

*Trimagnesic* or *neutral salt*, $\overset{''}{Mg}{}^3P^2O^8$. Formed by precipitating sulphate of magnesium with trisodic phosphate, or by boiling the dimagnesic salt with water. It retains 5 at. water at 100° (**Rammelsberg**), but becomes anhydrous on ignition. According to **Völcker** (Rep. Br. Assoc. 1862, p. 169) 100 pts. of water dissolve 0·0205 pt. of the recently precipitated, and 0·01 pt. of the ignited salt. It is readily soluble in acids, even after exposure to a white heat.

This salt is of frequent occurrence in plants, and forms a considerable proportion of the ash of the seed of cereal grasses, especially of wheat. It is present in smaller quantity in the bones of animals, and forms the chief constituent of many animal concretions, especially of bezoar stones.

**Wagnerite**, a rare mineral found in veins of quartz, traversing clay-slate in the valley of Höllengraben near Werfen in Saltzburg, is a phosphato-fluoride of magnesium, represented by the formula $Mg^3P^2O^8.MgF^2$. It occurs in monoclinic crystals having the orthodiagonal, clinodiagonal, and principal axis, as 1·1·045 : 1 : 0·78654, and the angle of the inclined axes = 71° 53′. $\infty P : \infty P = 95° 25'$; $oP : [P\infty] = 144° 25'$. Observed faces, $\infty P$, $+P$, $-P$, $-P2$, $+\frac{1}{2}P$, $\infty P2$, $[P2]$, and others. Most of the prismatic faces are deeply striated. Cleavage, parallel to $\infty P$ and the orthodiagonal, imperfect; parallel to $oP$ in traces. Hardness = 5 to 5·5. Specific gravity of a transparent crystal = 3·068; of an opaque crystal = 2·985 (**Rammelsberg**). The crystals are yellow, of various shades, with a vitreous lustre; streak white; translucent. Fracture uneven and splintery across the prism. Before the blowpipe it melts with great difficulty and only in thin splinters, giving off gas-bubbles, and forming a greenish-grey glass; when moistened with sulphuric acid, it colours the flame blue-green. With fluxes it gives a faint iron reaction, and melts with carbonate of sodium, effervescing but not dissolving.

The mineral has been analysed by **Fuchs** (Schw. J. xxxiii. 269) and Rammelsberg with the following results:

| | F | $P^2O^5$ | $Mg''O$ | $Ca''O$ | $Fe''O$ | $Mn''O$ | | |
|---|---|---|---|---|---|---|---|---|
| *a.* | 6·17 | 41·73 | 46·66 | . . | 4·50 | 0·45 | = | 99·51 (**Fuchs**). |
| *b.* | . . | 41·89 | 42·04 | 1·65 | 2·72 | 0·55* | | (**Rammelsberg**). |
| *c.* | . . | 40·23 | 38·49 | 4·40 | 3·31 | 0·96† | | ,, |
| *d.* | 9·36 | 40·61 | 46·27 | 2·38 | 4·59 | | = | 103·21 ,, |

The formula $3Mg''O.P^2O^5.Mg''F^2$ requires 11·73 per cent. fluorine, 43·83 phosphoric anhydride, 37·04 magnesia, and 7·41 magnesium (or 49·38 magnesia in all). The lime in the specimen analysed by Rammelsberg was present as carbonate.

**Lazulite** (iii. 477) is a phosphate of magnesium, iron (ferrosum), and aluminium.

8. ***Phosphates of Magnesium and Ammonium.***—1. *Ammonio-monomagnesic orthophosphate* $(NH^4)^2Mg''H^2P^2O^8.3H^2O$ separates in needle-shaped crystals on mixing warm and not too dilute solutions of magnesic sulphate and diammonic orthophosphate, and leaving the liquid to cool.

2. *Ammonio-dimagnesic Orthophosphate*, $(NH^4)^2\overset{''}{Mg}{}^2P^2O^8.12H^2O$.—This salt, the ordinary ammonio-magnesic phosphate, is produced when a magnesium salt mixed with sal-ammoniac is mixed with an alkaline orthophosphate and free ammonia, separating immediately from moderately strong solutions as an amorphous precipitate, which soon

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* After deduction of 2·68 silica.

† Alumina.

becomes heavy and crystalline; from dilute solutions it separates after some time only in small crystals which attach themselves to the sides of the vessel, especially on points presenting any roughness or inequality. It separates in this manner from extremely dilute solutions, thus affording a very delicate test either for magnesia or for phosphoric acid (iii. 752; iv. 542). The best mode of obtaining it in distinct crystals is to mix 600 pts. of hot water with 4 pts. of strong ammonia, and then add 7 pts. crystallised phosphate of sodium, 2 pts. sal-ammoniac, and 4 pts. sulphate of magnesium; the liquid, which is originally alkaline, becomes neutral after the separation of the crystals. (Graham.)

This salt is a frequent constituent of urinary calculi, the so-called fusible calculus consisting almost wholly of it: it is also found in intestinal concretions, especially in graminivorous animals. It is formed in the putrefaction of urine, and is precipitated therefrom on addition of ammonia in stellate groups of microscopic crystals; it sometimes separates spontaneously even from acid urine in three-sided prisms. Large crystals of it have been found in some varieties of guano, namely, from Patagonia and from Saldanha Bay on the coast of Africa, and in an old dung-pit at Hamburg; this native salt is called *Struvite* or *Guanite*.

The crystals are trimetric, having the axes $a : b : c = 0{\cdot}5429 : 1 : 0{\cdot}6233$; those of native struvite are six-sided prisms about an inch long, exhibiting the faces $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $\infty\breve{P}3$, $\bar{P}\infty$, $\frac{3}{2}\bar{P}\infty$, $\frac{1}{2}\bar{P}\infty$, $oP$, and hemimorphous from predominance of the face $\infty\breve{P}\infty$ on one side (Teschemacher, Phil. Mag. [3] xxviii. 546.—De la Provostage, Compt. rend. lviii. 442; see also Dana, ii. 413). They have a specific gravity of 1·65 – 1·7; hardness = 2; a vitreous lustre; are transparent and often coloured yellowish by impurities. The artificial salt generally forms a fine crystalline powder, or colourless, translucent, four-sided prisms.

The salt is tasteless and slightly soluble in pure water, 1 pt. of it dissolving in 15,300 pts. of cold water according to Fresenius; in 13,500 pts. according to Ebermayer (Compt. rend. xxxvii. 350). In presence of sal-ammoniac it is more soluble, 1 pt. of the salt dissolving in 7550 pts. of a liquid containing 1 pt. sal-ammoniac in 5 pts. water (Fresenius). In water containing free ammonia, on the contrary, it is less soluble than in pure water, 1 pt. requiring for solution 44,000 pts. of ammoniacal water (Fresenius). According to Ebermayer, the solubility diminishes as the proportion of ammonia in the water increases; thus—

| Mixture containing: | | Quantities required to dissolve 1 pt. of the Anhydrous Double Salt. |
|---|---|---|
| Water. | Aqueous Ammonia of specific gravity 0·961. | |
| 100 pts. | 25 | 31,000 pts. |
| 100 | 100 | 43,000 |
| 100 | 200 | 45,000 |
| 100 | 300 | 52,000 |
| Pure aqueous Ammonia of specific gravity 0·961. | | 60,000 |

The addition of sal-ammoniac renders the salt more soluble also in water containing free ammonia; phosphate of sodium does not appear to diminish the solubility.

The double salt dissolves easily in acids. At 100° it gives off 10 at. water without loss of ammonia; at a stronger heat the whole of the water and ammonia escape, the mass exhibits a vivid glow, and pyrophosphate of magnesium remains behind:

$$(NH^4)^2\overset{''}{Mg}{}^2P^2O^8 \;=\; \overset{''}{Mg}{}^2P^2O^7 + NH^3 + H^2O.$$

γ. ***Pyrophosphate of Magnesium***, $\overset{''}{Mg}{}^2P^2O^7.3H^2O$ (at 100°). This salt remains in the anhydrous state when ammonio-dimagnesic phosphate is ignited.

The hydrated salt is obtained by precipitating sulphate of magnesium with an alkaline pyrophosphate. The precipitate dissolves in excess of either of the salts which produce it, the solutions becoming turbid on boiling and remaining turbid when cold. The precipitated salt is white, amorphous, and bakes together in drying like hydrate of aluminium. It may be rendered crystalline by dissolving it in sulphurous acid and boiling the solution. It is very slightly soluble in water, but dissolves easily in nitric or hydrochloric acid. (Schwarzenberg.)

**Phosphates of Manganese.** α. *Metaphosphate*, $Mn''P^2O^6$.—Produced by evaporating a manganous salt with excess of phosphoric acid, heating the residue to 316°, in the same manner as for the preparation of the corresponding cupric salt (p. 560). It is reddish white, insoluble in water and dilute acids; does not melt at a red heat; is scarcely acted upon by sulphide of sodium or ammonium, even with aid of heat;

but is decomposed by digestion with carbonate of sodium, yielding dimetaphosphate of sodium; whence Fleitmann regards the manganous salt also as dimetaphosphate.

A solution of manganous chloride mixed with dimetaphosphate of ammonium and a little alcohol, deposits crystals of a hydrated salt, $Mn''P^2O^6.4H^2O$, which is insoluble in water and dilute acids, and gives off all its water on ignition. It is decomposed by heating with sulphuric acid and by fusion with alkaline carbonates. (Fleitmann.)

β. *Manganic Orthophosphate.*—When manganic oxide or finely divided pyrolusite is mixed with aqueous phosphoric acid, the liquid evaporated down, and the dry residue finally heated nearly to redness, a violet substance is formed, which is resolved by water into a dark red solution, and a peach-blossom-coloured insoluble powder, consisting of $Mn^2O^3.3P^2O^5.2H^2O$ or $Mn'''P^3O^9.H^2O$: therefore a metaphosphate. The red acid solution yields by evaporation light brown-red crystals of variable composition. (Hermann, Pogg. Ann. lxxiv. 303.)

Kobell (J. pr. Chem. lxxvi. 415; Jahresb. 1859, p. 656) recommends manganic phosphate for use in volumetric analysis in place of permanganate of potassium, as being more easily obtained. He prepares it by boiling down a mixture of finely divided pyrolusite and aqueous phosphoric acid, till the residue becomes syrupy and assumes a deep violet-blue colour; if not too strongly heated, it dissolves completely in water, and if diluted with six times its volume of water, it is as permanent as a solution of permanganate. It may be titrated in the same manner as the latter by means of a ferrous solution.

γ. *Manganous Orthophosphates.*—*Monomanganous salt*, $Mn''H^4P^2O^8.2H^2O$.—A solution of one of the two following salts in aqueous phosphoric acid yields this salt on evaporation in small prismatic easily soluble crystals, which give off half their water of crystallisation at 120°. Alcohol decomposes them, abstracting phosphoric acid and leaving the dimanganous salt.

The *dimanganous salt*, $\overset{''}{Mn}{}^2H^2P^2O^8.6H^2O$, is obtained by adding disodic orthophosphate to a solution of manganous sulphate acidulated with acetic, hydrochloric, or phosphoric acid, till the precipitate begins to be permanent; it then separates on standing in hard granular crystals (Heintz). It is also obtained in the crystalline form by precipitating a manganous salt with phosphate of sodium, mixing half the liquid with free acid till the precipitate dissolves, and then adding the other half (Bödecker); also by treating the trimanganous salt with half the quantity of phosphoric acid required to dissolve it.

The *trimanganous salt*, $\overset{''}{Mn}{}^3P^2O^8.7H^2O$, is formed by precipitating a neutral solution of a manganous salt with disodic orthophosphate. It is a white amorphous powder, which dissolves sparingly in water, easily in dilute acids, gives off 4 at. water at 100°, the remainder only at a red heat.

*Ammonio-manganous phosphate*, $\overset{''}{Mn}{}^2(NH^4)^2P^2O^8.2H^2O$.—This salt, analogous to the ordinary ammonio-magnesic salt dried at 100° (p. 570), is produced by the action of ammonia on recently precipitated trimanganous phosphate, or by precipitating a manganous salt with phosphate of sodium in presence of an ammonium salt and free ammonia. To obtain it crystallised, a solution of manganous chloride is precipitated in a flask with phosphate of sodium; hydrochloric acid is then added till the precipitate dissolves; and the solution is heated to boiling, and then mixed with excess of ammonia. The precipitate, which is amorphous at first, changes on standing for some time in the closed vessel into silvery laminæ usually having a reddish colour. (Otto.)

The salt is insoluble in water and in alcohol, easily soluble in dilute acids: it is decomposed by boiling with caustic but not with carbonated alkalis.

*Ferroso-manganous Phosphates.*—1. Triplite, a mineral from Limoges in France, has the composition $\left.\begin{matrix}2Fe''O\\2Mn''O\end{matrix}\right\}.P^2O^5 = \left.\begin{matrix}\frac{1}{2}Fe''O\\\frac{1}{2}Mn''O\end{matrix}\right\}.(\overset{''}{Fe}{}^{\frac{1}{2}}\overset{''}{Mn}{}^{\frac{1}{2}})^3P^2O^8$. It occurs in imperfectly crystalline masses, exhibiting three unequal cleavages in directions at right angles to each other, therefore trimetric. Hardness = 5·5. Specific gravity = 3·44—3·8. It has a brown colour, yellowish grey streak, and resinous lustre inclining to adamantine. Subtranslucent to opaque. Fracture small conchoïdal. Contains, according to Berzelius 32·61 per cent. $P^2O^5$, 31·95 $Fe''O$, 32·40 $Mn''O$ and 1·73 $Ca''O$; the formula requires 32·61 per cent. $P^2O^5$, 34·17 $Fe''O$ and 32·40 $Mn''O$.

Heterosite (iii. 151) and Hureaulite (iii. 176) are hydrated ferroso-manganous phosphates.

A *ferroso-manganous phosphato-fluoride* called Zwieselite, having in fact the composition of a fluorapatite in which the calcium is replaced by iron and manganese, is found at Zwiesel near Bodenmais in Bavaria, in crystalline masses, supposed to have a hexagonal structure isomorphous with that of apatite. It cleaves distinctly but imperfectly in three directions. Hardness = 5. Specific gravity = 3·97. Lustre greasy. Colour clove-brown, streak greyish-white. Fracture uneven or imperfect conchoïdal. It has been analysed by Fuchs (J. pr. Chem. xviii. 499) and Rammelsberg (*Mineralchemie*, p. 351), with the following results:—

| F | $P^2O^5$ | $Fe''O$ | $Mn''O$ | $SiO^2$ | | | |
|---|---|---|---|---|---|---|---|
| 3·18 | 35·60 | 41·56 | 20·34 | 0·68 | = | 101·36 | (Fuchs). |
| 6·00 | 30·33 | 41·42 | 23·25 | | = | 101 | (Rammelsberg). |

Rammelsberg's analysis leads to the formula $\left.\begin{matrix}\frac{2}{3}Fe''O \\ \frac{1}{3}Mn''O\end{matrix}\right\}^3.P^2O^5 + \left.\begin{matrix}\frac{2}{3}Fe'' \\ \frac{1}{3}Mn''\end{matrix}\right\}F^2$ or $(\frac{2}{3}Fe''.\frac{1}{3}Mn'')^3P^2O^5.(\frac{2}{3}Fe''\frac{1}{3}Mn'')F^2$, which requires 8·46 per cent. F, 31·60 $P^2O^5$, 42·73 $Fe''O$ and 20·77 $Mn''O$. Fuchs erroneously regarded the mineral as apatite having the calcium isomorphously replaced by iron and manganese, and thence called it *iron-apatite.*

*Lithio-ferroso-manganous Phosphates.*—1. Triphylline, from Bodenmais in Bavaria, is an isomorphous mixture of the orthophosphates of iron, manganese, and lithium. It mostly occurs massive, but sometimes in trimetric crystals, exhibiting the combination $\infty P\ .\ \infty\bar{P}2\ .\ \infty\breve{P}\infty\ .\ \breve{P}\infty\ .\ oP$. Angle $\infty P : \infty P = 93\frac{1}{2}^\circ : oP : \breve{P}\infty = 133^\circ$. The surfaces however are rather dull, and the angles not constant. Cleavage parallel to oP, sometimes perfect; parallel to $\infty P$ and one diagonal, imperfect, the latter least so. Hardness = 5. Specific gravity = 3·6. Subresinous, with greenish or bluish-grey colour, and greyish-white streak. Translucent in thin fragments. It decrepitates slightly when heated, giving off a small quantity of water, and acquiring a darker colour. Before the blowpipe it fuses very easily to a shining, dark grey, magnetic bead, colouring the flame bluish-green and sometimes reddish; with fluxes it gives the reactions of iron and manganese. It dissolves readily in acids; is imperfectly decomposed by caustic potash.

The first three of the following analyses of triphylline are by Rammelsberg (*Mineralchemie*, p. 323); the fourth is of a variety called *tetraphylline* or *perowskine*, from Tammela in Finland, by Berzelius and Nordenskiold; it differs from the Bodenmais mineral in exhibiting on the freshly broken surface a yellow colour, gradually becoming black.

| $P^2O^5$ | $Fe''O$ | $\overset{\prime\prime}{Mn}O$ | $Li^2O$ | $Na^2O$ | $K^2O$ | $Ca''O$ | $Mg''O$ | $SiO^2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 40·72 | 39·97 | 9·80 | 7·28 | 1·45 | 0·58 | . . | . . | 0·25 | = | 100·05 |
| 40·32 | 36·54 | 9·05 | 6·84 | 2·51 | 0·35 | 0·58 | 1·97 | . . | = | 98·16 |
| 44·19 | 38·21 | 5·63 | 7·69 | 0·74 | 0·04 | 0·76 | 2·39 | 0·40 | = | 100·05 |
| 42·6 | 38·6 | 12·1 | 8·2 | . . | . . | . . | 1·7 | . . | = | 103·2* |

Rammelsberg deduces from this third analysis the formula $\left.\begin{matrix}\frac{4}{5}Li^2O \\ \frac{1}{5}Mg^2O\end{matrix}\right\}^3.P^2O^5.$ $2\left[\left.\begin{matrix}\frac{7}{8}Fe''O \\ \frac{1}{8}Mn''O\end{matrix}\right\}^3.P^2O^5\right.$, requiring 44·81 per cent. $P^2O^5$, 39·76 $Fe''O$, 5·53 $Mn''O$, 7·37 $Li^2O$ and 2·53 magnesia. The first two analyses, which gave larger quantities of base, he supposes to have been made on samples which had perhaps lost some of their acid by weathering, or were mixed with small quantities of triplite (p. 572).

The following minerals are supposed to have been formed from triphylline or triplite by assumption of water and oxidation, the triphylline also sometimes losing its alkalis.

1. Black crystals from Norwich, Massachusetts, closely resembling triphylline in form and cleavage, but presenting considerable variation in their angles (for the measurements see Dana, *Mineralogy*, ii. 407). Hardness = 5·5. Specific gravity = 2·876. Streak brownish-red. Opaque. Brittle. Melts easily before the blowpipe with intumescence to a black mass. Mean of two analyses by Craw. (Sill. Am. J. [2] xi. 99).

2. *Alluaudite*, from Chanteloub near Limoges. Brown, cleaving like triplite. Hardness above 4. Specific gravity = 3·168 Dissolves in hydrochloric acid with evolution of chlorine. Analysis by Damour (Ann. Min. [4] xiii. 341).

| | $P^2O^5$ | $\overset{\prime\prime\prime}{Fe^2}O^3$ | $\overset{\prime\prime\prime}{Mn^2}O^3$ | MnO | CaO | $Na^2O$ | $Li^2O$ | $H^2O$ | $SiO^2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Norwich Crystals | 43·00 | 26·69 | 24·00 | . . | 1·79 | . . | 2·23 | 2·07 | 0·30 | = | 100·08 |
| Alluaudite | 41·25 | 25·62 | 1·06 | 23·08 | . . | 5·47 | . . | 2·65 | 0·60 | = | 99·73 |

Rammelsberg suggests for these minerals the formulæ:

$$(1)\quad (M^2O.P^2O^5).(\overset{\prime\prime\prime}{M^2}O^3.2P^2O^5) + aq.$$

$$(2)\quad (M^2O.P^2O^5).2(2\overset{\prime\prime\prime}{M}O^3.P^2O^5) + 4\ aq.;$$

but observes that it is very doubtful whether they are homogeneous.

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* The excess in this analysis is supposed to have arisen from an incorrect determination of the lithia.

(3.) Pseudotriplite, from Bodenmais in Bavaria; probably formed by oxidation of triphylline and removal of the alkalis by water. Slightly attacked by nitric acid. The first of the following analyses is by Fuchs; the second by Delffs (*Rammelsberg's Mineralchemie*, p. 332).

| $P^2O^5$ | $\overset{\prime\prime\prime}{Fe}{}^2O^3$ | $\overset{\prime\prime\prime}{Mn}{}^2O^3$ | $H^2O$ | $SiO^2$ | | |
|---|---|---|---|---|---|---|
| 35·70 | 48·17 | 8·94 | 5·30 | 1·40 | = | 99·51 |
| 35·71 | 51·00 | 8·06 | 4·52 | 0·71 | = | 100 |

Hence may be adduced the formula $\left.\begin{matrix}\frac{6}{7}\overset{\prime\prime\prime}{Fe}{}^2O^3\\ \frac{1}{7}Mn^2O^3\end{matrix}\right\}^3.2P^2O^5 + 2\text{ aq.}$

(4.) A mineral from Chanteloub, sometimes called Heterosite (iii. 161). Bluish-violet. Specific gravity = 3·41. Contains according to Rammelsberg, 32·28 per cent. $P^2O^5$, 31·46 $Fe^2O^3$, 30·01 $Mn^2O^3$ and 6·5 water, whence perhaps it is constituted according to the formula $5M^2O^3.3P^2O^5 + 5$ aq.

8. *Manganous Pyrophosphate*, $\overset{\prime\prime}{Mn}{}^2P^2O^7.3H^2O$, at 100°.—Obtained by precipitation as a white amorphous powder, which by solution in sulphurous acid and boiling, may be converted into nacreous crystalline laminæ. It is soluble in acids and in ammonia, insoluble in excess of the manganous salt, but easily soluble in the alkaline phosphate, and from this solution the manganese is not precipitated by sulphide of ammonium even after long standing.

**Phosphates of Mercury.** α. *Metaphosphates.*—Mercuric oxide heated with metaphosphoric acid, yields on cooling a salt which crystallises with great difficulty.

A solution of mercuric nitrate, mixed with ordinary vitreous metaphosphate of sodium, yields a white precipitate, which changes on agitation to a thick, heavy, oily mass.

Mercurous nitrate yields in like manner a dense white precipitate, which becomes resinous on boiling, and dissolves in excess of sodic metaphosphate.

A mercurous metaphosphate cannot be produced in the dry way; for on heating mercurous oxide with phosphoric acid, mercury volatilises and mercuric metaphosphate remains behind.

β. *Orthophosphates.*—The *trimercuric salt*, $\overset{\prime\prime}{Hg}{}^3P^2O^8$, is obtained as a heavy white powder by precipitating mercuric nitrate (not the chloride) with ordinary phosphate of sodium; also by digesting mercuric sulphate with a solution of the alkaline phosphate. It is insoluble in cold water, soluble in acids, including phosphoric acid; also in water containing ammonium-salts, especially the chloride, 6 pts of which dissolved in water effect the solution of 1 pt. of mercuric phosphate. It is decomposed by aqueous alkalis and alkaline carbonates, a small quantity of mercuric oxide being sometimes dissolved. The dry salt melts when heated to a dark yellow glass, which solidifies to an opaque mass on cooling. (*Handw. d. Chem.* vi. 375.)

*Trimercurous Phosphate*, $Hg^3PO^4$, is precipitated, on adding phosphate of sodium in excess to mercurous nitrate, as a white powder, mostly amorphous, but sometimes crystalline; soluble in excess of mercurous nitrate; insoluble in water and in aqueous phosphoric acid; resolved by boiling with water into mercuric phosphate and metallic mercury; decomposed in like manner by hydrochloric acid. When the dry salt is gently heated in a tube metallic mercury escapes, and mercuric phosphate remains as a residue, yellow while hot, white after cooling. (*Handw.*)

*Mercurous Phosphato-nitrate*, $Hg^3PO^4.HgNO^3.H^2O$.—Obtained by adding phosphate of sodium to excess of mercurous nitrate, as a yellow crystalline precipitate which is not decomposed by washing with cold water. (Gerhardt, Ann. Ch. Pharm. lxii. 81.)

γ. *Pyrophosphates.*—1. *Mercuric salts*, $\overset{\prime\prime}{Hg}{}^2P^2O^7$ (dried at 100°). A solution of mercuric nitrate forms with pyrophosphate of sodium a white precipitate which becomes yellowish-red on further addition of the alkali-salt, and is converted by an excess of the latter into a reddish-yellow basic compound. It is insoluble in water, easily soluble in acids, insoluble in excess of sodic pyrophosphate, quickly decomposed by potash (Gmelin). Mercuric chloride is not immediately precipitated by alkaline pyrophosphates, but after some time, or more quickly when heated, a red basic salt is precipitated. (*Handw.*, vi. 398.)

2. *Mercurous Pyrophosphate*, $Hg^4P^2O^7.H^2O$ (at 100°).—Mercurous nitrate forms with pyrophosphate of sodium a white crystalline precipitate, insoluble in water, soluble when recently precipitated in excess of the alkaline pyrophosphate, the solution depositing a black powder when boiled. The salt dried at 100° is blackened by solu-

tion of sodic pyrophosphate, but not dissolved. The salt when ignited leaves a residue of mercuric metaphosphate. (Schwarzenberg.)

**Phosphates of Molybdenum.** A solution of molybdic chloride yields with orthophosphate of ammonium, a light red flocculent precipitate, but the precipitation is not complete. A filtered solution of molybdic dioxide in aqueous phosphoric acid leaves, on evaporation, a red viscid mass consisting of an acid salt, soluble with red colour in ammonia; but the solution soon becomes turbid, and deposits the greater part of the salt; it becomes colourless on exposure to the air.

A solution of molybdous chloride forms, with disodic orthophosphate, a dark grey precipitate, soluble in excess of the molybdous chloride. A solution of molybdous hydrate in phosphoric acid yields, by spontaneous evaporation, a dark purple deliquescent mass, the ammoniacal solution of which is dark brown by transmitted, black and opaque by reflected light.

*Phosphomolybdic acid* has already been described (iii. 1037). The yellow phosphomolybdate of ammonium, precipitated on adding a small quantity of a soluble orthophosphate to a solution of molybdate of ammonium mixed with nitric or hydrochloric acid, contains, according to various authorities, from 3·14 to 3·82 per cent. $P^2O^5$, and 91·28 to 92·70 per cent. $MoO^3$. Zencker (Jahresb. 1853, p. 355) assigns to it the formula $(NH^4)^2O.5(H^2O.MoO^3) + 2(NH^4)H^2PO^4$. By mixing a syrupy solution of molybdic trioxide in hydrochloric acid with a small quantity of phosphoric acid, and saturating with potash, a mass of crystalline scales is obtained, consisting of a potassium-salt, having, according to Zencker, the composition $3(K^2O.MoO^3).2KH^2PO^4.9H^2O$ (see iii. 1037 and iv. 546).

**Phosphates of Nickel.** α. *Metaphosphate*, $Ni''P^2O^6$.—Obtained by evaporating a solution of nickel-sulphate in phosphoric acid and heating the residue to 316°. It is a greenish-yellow powder, insoluble in water and in dilute acids, and not decomposed by aqueous alkaline carbonates or sulphides even at the boiling heat, but decomposed by heating with strong sulphuric acid or by fusion with carbonate of sodium. (Maddrell.)

β. *Orthophosphate*, $\overset{\prime\prime}{Ni}{}^3P^2O^8.7H^2O$.—Light green precipitate insoluble in water, soluble in excess of the nickel-salt, easily soluble in acids; gives off water and turns yellow when heated.

The recently precipitated salt dissolves in aqueous ammonia, and on boiling the solution, or mixing it with alcohol, an ammonio-nickel phosphate is deposited in light blue-green or apple-green flocks. If the alcohol be carefully poured on the solution so as to form a layer on the surface, the double salt is gradually deposited in green crystalline grains.

γ. *Pyrophosphate*, $\overset{\prime\prime}{Ni}{}^2P^2O^7.6H^2O$ (at 100°), is obtained by precipitation as a light green powder, insoluble in water, easily soluble in acids, and separating in the crystalline state from the solution in sulphurous acid: it dissolves in ammonia and in excess of alkaline pyrophosphate, and the nickel is precipitated therefrom by sulphide of ammonium.

If the nickel-salt contains cobalt, the cobalt-pyrophosphate is deposited from the solution in sulphurous acid on boiling, before the nickel-salt, and on mixing the ammoniacal solution with alcohol, the cobalt-salt is precipitated alone.

**Phosphate of Osmium.** An osmious phosphate is produced by burning phosphide of osmium in contact with air, or dissolving osmious hydrate in aqueous phosphoric acid. It forms a dark blue-green mass nearly insoluble in cold water, but soluble with green colour in nitric acid.

**Phosphate of Palladium.** When aqueous phosphoric acid is boiled in contact with palladium, part of the metal dissolves, and phosphorous acid is likewise formed, which reduces a portion of the dissolved palladious oxide, so that as the liquid cools a film of metallic palladium forms on its surface.

Palladious nitrate yields a light yellow precipitate with alkaline orthophosphates.

**Phosphates of Potassium.** α. *Metaphosphates.*—Monopotassic orthophosphate heated nearly to redness is converted, without melting, into the metaphosphate $KPO^3$, which melts at a higher temperature without further alteration (Graham). The same salt is obtained by evaporating 2 pts. potassic chlorate with 1 pt. of syrupy phosphoric acid, strongly igniting the residue, and treating it with water: the metaphosphate then remains as a white powder (Maddrell). It is nearly insoluble in water, but is dissolved by acids either concentrated or dilute. Its solution in acetic acid gives precipitates with chloride of barium, acetate of lead, and nitrate of silver.

The *dimetaphosphate*, $K^2P^2O^6.H^2O$, is prepared by digesting anhydrous cupric dimetaphosphate with a solution of monosulphide of potassium containing but little sulphydrate, and heating the liquid to the boiling point. On adding a little alcohol to the filtrate, the dimetaphosphate separates in the form of a concentrated solution, which does not crystallise completely till after some time. The salt is soluble in 1·2 pts. of water either hot or cold; the solution has a saline, somewhat bitter taste. At 100° it gives off all its water without any molecular alteration of the residual salt, but at a low red heat it is converted into monometaphosphate, which melts at an incipient white heat, and solidifies in the crystalline form on rapid cooling. (Fleitmann.)

*Metaphosphates of Potassium and Ammonium.*—When 1 at. dimetaphosphate of potassium and 1 at. of the corresponding ammonium-salt are mixed and evaporated, the salt $K^3(NH^4)P^4O^{12}.2H^2O$ crystallises out first; afterwards a salt containing more ammonia, viz. $K^2(NH^4)^5.P^7O^{21}$, which, if thoroughly purified, would probably exhibit the composition $K(NH^4)^3P^4O^{12}$. The first salt contains the same proportion of crystallisation water as dimetaphosphate of potassium, and gives it all off at 150°. (Fleitmann.)

β. *Orthophosphates.*—The *monopotassic* or *di-acid salt*, $KH^2PO^4$, is obtained by mixing potassic hydrate or carbonate, or either of the two following salts, with sufficient aqueous phosphoric acid to produce a slight acid reaction. On evaporating the solution, the salt is deposited in large regular dimetric crystals, having a pure acid taste, easily soluble in water, but insoluble in alcohol. It undergoes no alteration at 200°, but at a low red heat it gives off its water, and is converted into metaphosphate.

The *dipotassic* or *mono-acid salt*, $K^2HPO^4$, is produced by mixing aqueous phosphoric acid with a sufficient quantity of alkali or alkaline carbonate to produce a slight alkaline reaction, and evaporating. It crystallises, according to Berzelius, in irregular forms; according to Graham it is uncrystallisable. It is easily soluble in water, insoluble in alcohol, and is converted into pyrophosphate by ignition.

The *tripotassic* or *neutral salt*, $K^3PO^4$, is prepared by igniting phosphoric acid or either of the preceding salts with the requisite quantity of potassic hydrate or carbonate. By solution and evaporation it may be crystallised in needles which are very soluble in water, but not deliquescent. The dry salt is permanent in the air; the solution absorbs carbonic acid (Graham). When strongly heated it melts to an enamel-like mass.

*Baryto-potassic phosphate.*—By igniting 1 at. barytic pyrophosphate, $Ba^2P^2O^7$, with 1 at. potassic carbonate, a mass is obtained which, when washed with water, yields a solution containing potash and phosphoric acid, while the residue contains the salt $Ba''KPO^4$, together with a large quantity of tribarytic phosphate.

*Calcio-potassic phosphate*, $Ca''KPO^4$, is formed by igniting together equivalent quantities of potassic carbonate and dicalcic phosphate. (H. Rose.)

*Magnesio-potassic phosphate*, $Mg''KPO^4$, obtained in like manner, is sparingly soluble in water, and may be completely washed with dilute aqueous ammonia. (H. Rose.)

γ. *Pyrophosphates of Potassium.*—The *dipotassic* or *acid salt*, $K^2H^2P^2O^7$, is prepared by dissolving the neutral salt in acetic acid, and adding alcohol; it then separates as a syrup, which must be washed several times with alcohol to remove the potassic acetate, and then dried over oil of vitriol. It is white, and very deliquescent. The aqueous solution is acid, and is not decomposed by boiling. (Schwarzenberg.)

The *tetrapotassic* or *neutral salt*, $K^4P^2O^7$, is formed by the ignition of dipotassic orthophosphate; but the residue when dissolved in water takes up basic water, and is reconverted into orthophosphate. The neutral pyrophosphate may, however, be obtained in a permanent state by treating an alcoholic solution of potash with a slight excess of ordinary phosphoric acid, and afterwards adding alcohol till the liquid becomes milky; in the course of 24 hours a dense acid syrup separates, which is a mixture of the di- and tetra-potassic orthophosphates. The syrupy mixture is then evaporated to dryness in a platinum dish and ignited, whereby a mixture is obtained consisting of pyrophosphate and metaphosphate of potassium, which can readily be separated, in consequence of the insolubility of the latter salt in water. Pyrophosphate of potassium, after ignition, forms a white fused mass, which deliquesces very rapidly in the air; its aqueous solution has an alkaline reaction, and may be boiled without being converted into orthophosphate. This change takes place, however, when the solution of the salt is boiled with caustic potash. When a syrupy solution of pyrophosphate of potassium is evaporated over oil of vitriol, it solidifies to a brilliant white mass consisting of $K^4P^2O^7.3H^2O$. One atom of water is driven off below 100°, but the salt is rendered anhydrous only at a temperature of 300°. (Schwarzenberg.)

*Ammonio-potassic pyrophosphate*, $2K^2(NH^4)HP^2O^7.H^2O$.—This salt remains when monopotassic pyrophosphate is saturated with ammonia, and the concentrated solution is evaporated over a mixture of quicklime and sal-ammoniac. It is white, deliquescent, and very soluble in water, forming an alkaline solution, which decomposes on boiling,

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with evolution of ammonia, ultimately leaving nothing but monopotassic pyrophosphate. (Schwarzenberg.)

*Chromico-potassic pyrophosphate.*—Chromic pyrophosphate dissolves in excess of potassic pyrophosphate, forming a green solution which is not precipitated by sulphydric acid or sulphide of ammonium.

*Cuprico-potassic pyrophosphate*, $Cu''K^2P^2O^7.H^2O$ (Persoz).—Cupric pyrophosphate dissolves in excess of the potassic salt, but the resulting double salt has not been obtained in the solid state, the solution when evaporated depositing cupric pyrophosphate. Persoz has, however, determined the composition of the dissolved salt by mixing a titrated solution of cupric nitrate with a titrated solution of potassic pyrophosphate till the precipitate which is formed at first redissolves.

A piece of iron immersed in the aqueous solution of the double salt becomes covered in a few days with microscopic crystals of metallic copper; in like manner zinc precipitates the copper from this solution, but slowly and imperfectly.

**Phosphate of Rhodium.** Rhodic oxide, mixed with phosphoric acid and heated to redness, yields a brown mass, from which water removes the excess of acid, but at the same time takes up a portion of the salt, acquiring thereby a dark brown colour, changing to light yellow on dilution.

**Phosphates of Silver.** α. *Metaphosphates.*—The *dimetaphosphate*, $Ag^2P^2O^6$, is obtained by precipitating nitrate of silver with the corresponding sodium-salt, as a crystalline powder, or in small distinct crystals, according to the degree of concentration of the solution used. It is slightly soluble in water, and melts when heated to a transparent glass, which is insoluble in water.

The *trimetaphosphate*, $Ag^3P^3O^9.H^2O$, separates gradually from a moderately concentrated mixture of silver nitrate with sodic trimetaphosphate, in crystals apparently monoclinic, soluble in 60 pts. of cold water, and separating unaltered on evaporating the solution acidulated with nitric acid. It gives off its water at 100° (not over oil of vitriol at ordinary temperatures), and when about half the water has gone off (about 1½ per cent.) the remaining salt is soft, has an acid reaction, and perhaps consists of hexmetaphosphate.

The trimetaphosphate has a great tendency to form double salts, so that the crystals obtained as above always contain a certain quantity of sodium-salt, unless a large excess of silver-nitrate has been used in preparing them.

*Hexmetaphosphate*, $Ag^6P^6O^{18}$, separates in shining crystals when oxide of silver is melted with excess of phosphoric acid and the mass is left to cool slowly. Formed also by precipitating a solution of recently ignited metaphosphoric acid in ice-cold water with nitrate of silver. It is white, insoluble in water, becomes soft and semi-fluid at 102°, and melts to a transparent glass at a higher temperature. It is decomposed by sulphide of sodium, yielding Graham's deliquescent metaphosphate of sodium. By prolonged boiling with water, it gives up part of its acid, and is converted into a ropy mass, consisting, according to Berzelius, of $3Ag^2O.2P^2O^5$, or $Ag^6P^4O^{13}$.

β. *Orthophosphates.*—The *di-argentic* salt, $Ag^2HPO^4$, is produced by dissolving the tri-argentic salt in phosphoric acid, or by mixing nitrate of silver with a large excess of phosphoric acid and evaporating (Berzelius), and often separates on mixing a solution of the tri-argentic salt in phosphoric acid with ether (Schwarzenberg). By evaporation of the acid solution, it is obtained in colourless crystalline laminæ. It is immediately resolved by contact with water into the tri-argentic salt and free phosphoric acid.

The *tri-argentic salt*, $Ag^3PO^4$, is obtained by precipitating nitrate of silver with any alkaline orthophosphate. It is a lemon-yellow powder, the colour of which affords a characteristic test for orthophosphoric acid, the other two modifications giving white precipitates (pp. 538, 539, 542). It is insoluble in water, but easily soluble in acids, even in acetic acid; also in aqueous ammonia, and is deposited on evaporating the ammoniacal solution in yellow crystalline grains. It is blackened and decomposed by exposure to light, assumes a transient dark orange-red colour when heated, and melts at a strong red heat.

γ. *Pyrophosphate*, $Ag^4P^2O^7$ or $2Ag^2O.P^2O^5$.—Formed by precipitating nitrate of silver with either acid or neutral pyrophosphate of sodium, the supernatant liquid being neutral in either case. It is a white powder, of specific gravity 5·306 at 75°; contains no water; fuses somewhat below a red heat, without any decomposition, and forms a dark brown liquid, which on cooling solidifies to a white, radiated mass; assumes a reddish colour on exposure to light. When boiled with ordinary phosphate of sodium, it is immediately decomposed, yielding yellow tri-argentic phosphate and aqueous pyrophosphate of sodium: probably in this manner:

$$3Ag^4P^2O^7 + 4Na^2HPO^4 = 4Ag^3PO^4 + Na^4P^2O^7 + 2Na^2H^2P^2O^7.$$

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According to this, the water should contain both mono- and di-sodic pyrophosphate. Pyrophosphate of silver dissolves readily in cold nitric acid; but when boiled with either nitric or sulphuric acid, it is converted into the orthophosphate, so that the solution gives a yellow precipitate on addition of ammonia. Aqueous hydrochloric acid converts it into chloride of silver and free phosphoric acid. It dissolves with tolerable facility in ammonia, and is thrown down unchanged by acids. It is insoluble in acetic acid, and not altered by boiling with water (Stromeyer); insoluble in solutions of the pyrophosphates; very slightly soluble in silver-nitrate. (Schwarzenberg.)

δ. *Fleitmann and Henneberg's Silver-phosphates.*—These salts are obtained by precipitating the corresponding sodium-salts (p. 537) with nitrate of silver. The salt $Ag^6P^4O^{13}$ or $3Ag^2O.2P^2O^5$ dissolves in a large excess of the sodium-salt; it is insoluble in water, but is decomposed by prolonged washing with water, phosphoric acid dissolving out. It melts at a moderately high temperature. It is perhaps identical with the salt which Berzelius obtained by prolonged boiling of di-argentic phosphate with water (p. 576).

The salt $Ag^{12}P^{10}O^{31}$ or $6Ag^2O.5P^2O^5$ is easily soluble in excess of the corresponding sodium-salt.

**Phosphates of Sodium.** α. *Metaphosphates*, $n$NaPO$^3$.—Salts having this composition obtained by ignition of disodic pyrophosphate, $Na^2H^2P^2O^7$, or monosodic orthophosphate, $NaH^2PO^4$, or sodio-ammonic orthophosphate (microcosmic salt), $Na(NH^4)HPO^4$, and most advantageously from the last-mentioned, which is easily prepared pure. The resulting metaphosphates, as first shown by Graham, exhibit considerable diversity of character, according to the degree of heat applied and the quickness or slowness of the rate of cooling—differences which, as already observed, are attributed to polymeric modifications (p. 538).

Monosodic pyrophosphate and orthophosphate, when heated for some time to 200°—250°, give off nearly all their water of crystallisation, and the remaining salt, after being heated to about 315°, retains scarcely one-third per cent. water. If it be then treated with water after cooling, the greater part dissolves as pyrophosphate, while a small quantity of metaphosphate remains behind. After the salt has been heated more strongly and for some minutes to near redness, the residue is for the most part insoluble, and consists of mono-metaphosphate. When strongly ignited it melts, and after very slow cooling yields a crystallisable salt containing sodic tri-metaphosphate; by rapid cooling, on the other hand, it is converted into vitreous hexmetaphosphate. In like manner microcosmic salt, when exposed to a gradually increasing temperature, first gives off crystallisation-water and ammonia, leaving a very acid soluble salt, consisting chiefly of disodic pyrophosphate; but on increasing the heat, more water goes off, and there remains a metaphosphate which melts at a red heat.—Dimetaphosphate and tetrametaphosphate of sodium are obtained from the corresponding copper and lead-salts by double decomposition.

1. The *monometaphosphate*, $NaPO^3$, obtained as above, or by fusing 2 pts. nitrate of sodium with 1 pt. of syrupy phosphoric acid at a strong heat, and washing out the product with cold water, is a dense white powder, nearly insoluble in water, even at the boiling heat, but easily dissolved by acids (Maddrell). By boiling with caustic alkalis it is slowly converted into orthophosphate.

2. *Dimetaphosphate*, $Na^2P^2O^6.2H^2O$.—Obtained by digesting cupric dimetaphosphate (p. 560) with a warm solution of monosulphide of sodium, filtering when the solution retains only a slight alkaline reaction, evaporating in contact with the air, dissolving the residue in water, and gradually adding an equal volume of alcohol of 80 per cent. It then separates in concentric groups of long needles. This salt dissolves in 7·2 pts. water, either hot or cold, forming a neutral solution, which may be kept for months without alteration in the cold, but is converted by prolonged boiling into orthophosphate without passing through the intermediate stage of pyrophosphate. It gives off all its water at 100°; the dry salt absorbs water from the air, and becomes hot when mixed with water. It separates unaltered from a solution in caustic soda on evaporation, and from solution in hydrochloric acid on addition of alcohol; but when heated with acids, especially with strong sulphuric acid, it yields orthophosphoric acid. (Fleitmann.)

*Sodio-ammonic Dimetaphosphate*, $Na(NH^4)P^2O^6.H^2O$, crystallises on adding alcohol to a solution of the dimetaphosphates of sodium and ammonium in equivalent proportions. The crystals resemble those of the sodio-potassic salt, are less soluble in water than di-metaphosphate of ammonium, but more soluble than the sodium-salt. It gives off its water at 100°. (Fleitmann.)

*Sodio-potassic dimetaphosphate*, $NaKP^2O^6.H^2O$, separates as a crystalline powder on mixing the concentrated solutions of the component salts in equivalent proportion; also on mixing the potassium-salt with chloride of sodium, or the sodium-salt with chloride of potassium. Dilute solutions yield the double salt in larger crystals by spontaneous evaporation. It dissolves in 24 pts. of cold water. The crystals do not give off all their water of crystallisation at 150°; at higher temperatures the salt melts, and is converted on cooling into transparent easily soluble hexmetaphosphate. (Fleitmann.)

*Sodio-argentic dimetaphosphate*, $NaAgP^2O^6$, separates gradually from a solution of silver-nitrate mixed with excess of the sodium-salt, in beautiful, transparent, monoclinic crystals. When, on the contrary, an excess of silver-nitrate is used, smaller crystals are obtained consisting of pure argentic dimetaphosphate. (Fleitmann and Henneberg.)

3. *Trimetaphosphate of Sodium*, $Na^3P^3O^9.6H^2O$ or $3Na^2O.3P^2O^5.12H^2O$ (crystallisable metaphosphate), is formed by exposing microcosmic salt to a moderate heat (Graham), or by slow cooling of the strongly heated and fused salt (Fleitmann and Henneberg). A considerable mass of the salt, left to cool very slowly, becomes beautifully crystalline, and if then dissolved in a moderate quantity of warm water, yields a milky liquid, which separates on standing into two layers, the larger of which yields the crystalline salt on evaporation. The finest crystals are obtained by leaving the concentrated solution to evaporate in shallow vessels. The crystals are oblique rhombic prisms, having a cooling saline taste, soluble in 4·5 pts. of cold water, sparingly soluble in aqueous alcohol, insoluble in absolute alcohol. The aqueous solution is permanent in the cold, but turns acid on boiling, and is quickly converted into acid orthophosphate; the same change is more quickly produced by dilute acids. The crystals do not melt in their water of crystallisation when heated. At 100°, or in vacuo over oil of vitriol, they give off $\frac{11}{12}$ of their water, the last portion being expelled only at a much higher temperature.

Trimetaphosphate of sodium forms soluble double salts with the two corresponding salts of the alkaline earth-metals and the diatomic heavy metals.

*Sodio-barytic trimetaphosphate*, $Na^2\overset{''}{Ba}{}^2P^6O^{18}.H^2O$, separates in stellate groups of crystals from a filtered solution of 1 pt. chloride of barium and 2 to 3 pts. trimetaphosphate of sodium. It is somewhat more soluble in water than the pure barium-salt (p. 553). The crystals give off 5 at. water at 100°, the rest without tumefaction at a stronger heat. The slightly ignited unfused mass is insoluble in water, but becomes easily soluble after fusion.

4. *Tetrametaphosphate of Sodium*, $Na^4P^4O^{12}$ with 3 or 4 at. $H^2O$, or $4Na^2O.4P^2O^5$ with 6 or 8 at. $H^2O$.—This salt is prepared by digesting the corresponding lead-salt with monosulphide of sodium. The action takes place quickly and with rise of temperature, the mixture swelling up and solidifying to a coherent elastic cake consisting of sodic tetrametaphosphate mixed with finely divided sulphide of lead, and the liquid remaining gummy even when diluted with 100 times its bulk of water, so that it can scarcely be filtered. By adding alcohol to the dilute solution, the salt is precipitated as a colourless elastic ropy mass, like caoutchouc. The solution is neutral, and dries up by spontaneous evaporation to a transparent, fissured, non-hygroscopic mass. The salt melts when heated, and is converted into hexmetaphosphate of sodium.

Tetrametaphosphate of sodium forms, with the salts of the alkaline earth-metals, insoluble elastic compounds, which by prolonged contact with water are converted into orthophosphates. (Fleitmann.)

*Sodio-cupric tetrametaphosphate*, $Na^4\overset{''}{Cu}{}^2P^8O^{24}$, is obtained by mixing the dimetaphosphates of copper and sodium, adding one-fourth as much free phosphoric acid as the two salts together contain, evaporating, and heating the dry residue to 300°.

*Sodio-magnesic metaphosphate*, $Na^2\overset{''}{Mg}P^4O^{12}$.—When phosphoric acid prepared from bones and freed from lime and sulphuric acid (p. 580) is evaporated down, and then heated for some time to 310°, metaphosphate of magnesium separates out first, and then, after longer heating, the sodio-magnesic salt, as a white powder, insoluble in water, hydrochloric acid and nitromuriatic acid, and soluble only in strong sulphuric acid (Maddrell). This salt has the composition of a di- or tetrametaphosphate, but the particular modification to which it belongs is not exactly known.

When sulphate of *cobalt* is heated to 316° with impure phosphoric acid containing sodic metaphosphate. A double salt, containing $Na^2\overset{''}{Co}{}^3P^8O^{24}$, separates as a powder of a fine rose colour, insoluble in water and in acids, even in strong sulphuric acid. A *nickel*-salt of analogous composition is obtained in like manner as a greenish powder, soluble only in strong sulphuric acid.

5. *Hexmetaphosphate of Sodium*, $Na^6P^6O^{18}$ or $6Na^2O.6P^2O^5$ (*deliquescent* or *vitreous metaphosphate;* Graham's *metaphosphate*). This salt, obtained by rapid cooling of the melted mass (p. 577), forms an amorphous, colourless glass which quickly absorbs moisture from the air and deliquesces. It dissolves easily in water and in alcohol, forming slightly acid solutions. When dried in the air at 30°, it becomes viscid and dries up to a transparent gum. The salt dried in vacuo contains 1 at. soda to more than 1¼ at. water (or 1 at. Na to 1¼ at. H.), and it still retains 1 at. water after drying

at 100°, but is then converted into disodic pyrophosphate, $Na^2H^2P^2O^7$. The aqueous solution does not undergo any change either in the cold or when boiled either alone or with caustic soda. (Graham.)

*Sodio-ammonic Hexmetaphosphate.*—When the solution of the salt just described is evaporated with sal-ammoniac and then mixed with alcohol, this double salt separates as a syrup, which may be purified by solution in water and reprecipitation with alcohol. It contains soda and ammonia in proportions varying between 1 : 1 and 5 : 1. (Fleitmann.)

β. *Orthophosphates of Sodium.*—The *monosodic salt*, $NaH^2PO^4.H^2O = \left.\begin{matrix}Na^2O\\2H^2O\end{matrix}\right\}P^2O^5.2H^2O$, is obtained by mixing the solution of the disodic salt with phosphoric acid till it no longer precipitates chloride of calcium. The solution concentrated and cooled deposits the salt in rather large crystals belonging to the trimetric system. The more ordinary form has the axes $a : b : c = 0{\cdot}9342 : 1 : 0{\cdot}9573$. Angle $\infty P : \infty P = 86° 6'$; $\breve{P}\infty : \breve{P}\infty$ (basal) $= 91° 24'$. The dominant combination is $\infty P . oP$ with the faces $\bar{P}\infty$, $P$, $\infty\breve{P}\infty$, and others subordinate. Sometimes, however, the salt crystallises in another form, also trimetric and isomorphous with monosodic arsenate, $NaH^2AsO^4.H^2O$. In this form the axes $a : b : c = 0{\cdot}8170 : 1 : 0{\cdot}4988$. Angle $P : P$ (brachyd.) $= 133° 48'$ : $P : P$ (macrod.) $= 122° 38'$; $P : P$ (basal) $= 76° 38'$; $\infty P : \infty P = 78° 30'$; $\breve{P}\infty : \breve{P}\infty$ (basal) $= 53° 7'$; $2\breve{P}\infty, 2\breve{P}\infty$ (basal) $= 83° 59'$. Principal faces $\infty P$, $P$, with $\breve{P}\infty$ and $2P\infty$ subordinate. The salt is therefore dimorphous (Kopp). By rapid crystallisation of a strongly concentrated solution, or from a solution of the disodic salt mixed with nitric acid, it separates in crystals.

The crystallised salt has a specific gravity of 2·040. It gives off all its crystallisation water at 100°, melts at 204°, giving off 1 at. basic hydrogen, and being converted into pyrophosphate, and at 235° it gives off the last atom of hydrogen, leaving a residue of metaphosphate. It is easily soluble in water, insoluble in alcohol. The solution forms a yellow precipitate with silver-nitrate, but the precipitation is not complete, as the nitric acid which is set free holds a portion of the silver phosphate in solution.

*Disodic Orthophosphate* or *Monoacid Phosphate of Sodium*, $Na^2HPO^4$ or $\left.\begin{matrix}Na^2O\\H^2O\end{matrix}\right\}P^2O^5$, also called *ordinary* or *neutral phosphate of soda; sal mirabile perlatum.*—This salt occurs in the blood, especially in that of poultry, and in urine. It is easily prepared by adding caustic soda or sodic carbonate to orthophosphoric acid till the liquid becomes slightly alkaline. It is obtained in larger quantities from bone-phosphoric acid, which for this purpose must be free from excess of sulphuric acid, but may contain lime or magnesia; 3 pts. of burnt bones are digested for about 24 hours with 2 pts. sulphuric acid and 24 pts. water; the resulting paste is washed with warm water, and the liquid is mixed with sufficient carbonate of sodium to produce a slight alkaline reaction. The lime and magnesia are thereby precipitated as trimetallic phosphates, any arsenious or arsenic acid that may be present being precipitated at the same time. The solution is then evaporated to the crystallising point, the more soluble foreign salts remaining in solution, and the crystals of disodic orthophosphate which separate are purified by solution and recrystallisation.

The crystals thus obtained contain 12 or 24 at. water $= Na^2HPO^4.12H^2O$ or $\left.\begin{matrix}2Na^2O\\H^2O\end{matrix}\right\}P^2O^5.24H^2O$. They are monoclinic prisms, having the axes $a : b : c = 0{\cdot}5773 : 1 : 0{\cdot}8211$. Angle of inclined axes $= 58° 30'$. $\infty P : \infty P$ (orthod.) $= 112° 10'$; $+P\infty : c = 70° 42'$; $+2P\infty : c = 37° 17'$; $oP : \infty P = 73° 3'$. Ordinary combination $\infty P . oP . +P . +2P\infty$, like figure 295 (Crystallography, ii. 154). Isomorphous with disodic arsenate, $Na^2HAsO^4.12H^2O$. The crystals are larger and better developed when they contain a small quantity of sodic carbonate.

A solution of the salt left to evaporate at 33° deposits crystals containing $Na^2HPO^4.7H^2O$ or $\left.\begin{matrix}2Na^2O\\H^2O\end{matrix}\right\}P^2O^5.14H^2O$. These crystals are monoclinic, having the axes $a : b : c = 0{\cdot}8271 : 1 : 1{\cdot}099$. Angle of inclined axes $= 83° 0'$. Angle $\infty P : \infty P$ (orthod.) $= 101° 14'$; $\infty P2 : \infty P2$ (orthod.) $= 62°$; $+P\infty : c = 45° 27'$; $oP : \infty P = 85° 34'$. Combination $\infty P . oP . \infty P\infty . [\infty P\infty] . +P . -P . +P\infty$. Cleavage parallel to $\infty P\infty$. The crystals are isomorphous with those of the corresponding sodic arsenate, $Na^2HAsO^4.7H^2O$. They do not effloresce on exposure to the air.

The crystals, $Na^2HPO^4.12H^2O$, have a specific gravity of 1·525 (Schiff, Jahresb. 1859, p. 16); they melt in their water of crystallisation at 35°, and the salt after fusion and solidification has a specific gravity of 1·586 at 8°. The crystals expand in the ratio of 1 : 1·001 between 0° and 20°; and of 1 : 1·005 between 0° at 35°; at the moment of fusion the volume increases by 5·1 per cent., so that the volume of the liquid salt at 35° is to the original volume at 0° as 1·056 : 1 (H. Kopp, Jahresb. 1855, p. 45). The crystals, when exposed to the air at ordinary temperatures, effloresce without disintegrating; at a gentle heat, even at 30°—40°, and likewise in vacuo over oil of vitriol, they gradually give off all their water of crystallisation, and the anhydrous salt, if exposed to moist air, gradually takes up 7 at. water. The specific gravity of the anhydrous salt, $Na^2HPO^4$, is 1·619 (Schiff). When heated to redness it gives off its basic hydrogen and is reduced to neutral sodic pyrophosphate.

The crystals with 12 (or 24) at. water dissolve in 4 pts. of cold and 2 pts. of hot water; a boiling saturated solution contains 112 pts. of the crystallised salt to 100 pts. water, and boils at 106·6 (Liebig). According to Ferrein (Jahresb. 1858, p. 117) 1 pt. of the crystallised salt dissolves in 11·73 pts. water at 13°, and the salt is soluble in almost all proportions of boiling water. According to Neese (Jahresb. 1863, p. 180), 1 pt. of the salt dissolves in 6·7 pts. water at 15°, in 5·8 pts. at 20°, and in 3·2 pts. at 25°. The solution saturated at 15° does not deposit any crystals after standing for eighteen hours at 12°. Hence Neese regards Liebig's statement regarding the solubility of the salt as more correct than that of Ferrein; Wittstein (Arch. Pharm. cxv. 43) regards the latter as the more exact.—The 7- or 14-hydrated salt $Na^2HPO^4.7H^2O$ or $2Na^2O.H^2O.P^2O^5 + 14$ aq. dissolves, according to Neese, in 8 pts. water at 23°. According to Poggiale (J. Pharm. [3] xliv. 273; Jahresb. 1863, p. 181), 100 pts. water at various temperatures dissolve the following quantities of the salt dried at 100°:—

| Temperatures. | Weight of salt $Na^2HPO^4$ dissolved. | Temperatures. | Weight of salt $Na^2HPO^4$ dissolved. |
|---|---|---|---|
| 0° | 1·55 | 60° | 55·29 |
| 10 | 4·10 | 70 | 68·72 |
| 20 | 11·08 | 80 | 81·29 |
| 30 | 19·95 | 90 | 95·02 |
| 40 | 30·88 | 100 | 108·20 |
| 50 | 43·31 | 106·2 | 114·43 |

According to Schiff (Ann. Ch. Pharm. cviii. 326; Jahresb. 1858, p. 38) the densities of solutions of various strengths are as follows:—

| Percentage of $Na^2HPO^4.12H^2O$ in solution. | Density of solution at 19°. |
|---|---|
| 10·59 | 1·0442 |
| 6·99 | 1·0292 |
| 5·29 | 1·0220 |
| 4·66 | 1·0198 |
| 3·50 | 1·0160 |
| 2·33 | 1·0114 |
| 1·16 | 1·0067 |

Ordinary phosphate of sodium has a cooling saline taste, not so unpleasant as that of Glauber's salt, and is often used instead of the latter as a purgative. The commercial salt frequently contains small quantities of sulphate and chloride, also traces of arsenic derived from the sulphuric acid used in its preparation from bones.

*Trisodic orthophosphate*, $Na^3PO^4.12H^2O$ or $3Na^2O.P^2O^5.24H^2O$.—This salt is obtained by mixing a solution of the preceding with caustic soda and evaporating to the crystallising point; or by igniting dry disodic orthophosphate or pyrophosphate with the requisite quantity of sodic carbonate, dissolving the mass in water, and crystallising. It may be purified by recrystallisation from 2 parts of boiling water.

The crystals are thin six-sided prisms with truncated end-faces; they have a specific gravity of 1·618 (Schiff); are permanent in dry air; melt in their water of crystallisation at 77°. The salt dried at 100° still retains 1 at. water (out of 24 at.), which it gives off only at a red heat. It does not melt even at a full red heat, but attacks glass strongly at that temperature. The crystals dissolve in 5 pts. water at 15°. The densities of solutions of various strengths are, according to Schiff (Ann. Ch. Pharm. cxiii. 183; Jahresb. 1859, p. 41), as follows:—

| Percentage of $Na^3PO^4.12H^2O$. | Density of solution at 15°. |
|---|---|
| 22·03 | 1·1035 |
| 17·60 | 1·0812 |
| 11·00 | 1·0495 |
| 8·80 | 1·0393 |
| 4·40 | 1·0193 |

The solution when exposed to the air absorbs carbonic acid, which, as well as other weak acids, abstracts the third atom of base. Chlorine, bromine, and iodine likewise

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act upon the third atom of soda as on free soda. When a neutral silver-solution is precipitated by trisodic phosphate, the liquid remains neutral.

*Phosphato-fluoride of Sodium*, $Na^3PO^4.NaF$, is produced by fusing together 4 pts. of disodic pyrophosphate, 2⅔ pts. sodic carbonate, and 1 pt. fluor-spar, and digesting the fused mass with warm water; also by digesting pulverised cryolite for several days with a solution of ordinary phosphate of sodium and caustic soda, and leaving the solution to evaporate; or by mixing a solution of fluoride of sodium with ordinary phosphate and caustic soda. Either of these solutions, after concentration over the water-bath, deposits the phosphato-fluoride in hard, limpid, regular octahedrons modified with faces of the cube and rhombic dodecahedron. It has a specific gravity of 2·2165 at 25°, dissolves in 8·31 pts. water at 25° (the solution having a density of 1·0329), and in 1·74 pts. water at 70° (specific gravity of solution = 1·091). The solution when boiled down deposits fluoride of sodium (Briegleb, Ann. Ch. Pharm. xcvii. 95; Jahresb. 1855, p. 338).

*Sodio-ammonic Orthophosphate*, $Na(NH^4)HPO^4.4H^2O$ or $\left.\begin{matrix}Na^2O\\(NH^4)^2O\\H^2O\end{matrix}\right\}P^2O^5.8H^2O.$

***Phosphorus-salt, Microcosmic salt, Sal urinæ nativum s. fusibile.***—This salt occurs abundantly in human urine, at least after putrefaction, and may be prepared therefrom; it is found also mixed with the carbonates and phosphates of calcium and magnesium in guano from Ichaboe; the salt from this source is called stercorite by Herapath. It is formed on mixing disodic orthophosphate with phosphate of ammonium or other ammoniacal salt, or monosodic orthophosphate with ammonia, and may be easily prepared by dissolving 5 pts. of ordinary crystallised disodic orthophosphate, and 2 pts. phosphate of ammonium in a small quantity of hot water, and crystallising, or 6 to 7 pts. of the crystallised sodium-salt and 1 pt. sal-ammoniac in 2 pts. of boiling water; the sodio-ammonic salt then crystallises out on cooling, while chloride of sodium remains in solution: $Na^2HPO^4 + NH^4Cl = Na(NH^4)HPO^4 + NaCl$. It may be freed from chloride of sodium by recrystallisation from a small quantity of boiling water containing a little free ammonia.

The crystals are monoclinic prisms, isomorphous with those of the corresponding arsenate. Axes $a : b : c = 0·3469 : 1 : 0·3236$. Angle of inclined axes = 80° 42'. $\infty P : \infty P$ (orthod.) = 141° 16'; $-2P\infty : c$ = 50° 43'; $+2P\infty : c$ = 63° 51'; $+4P\infty : c$ = 41° 8'; $oP : \infty P$ = 86° 56'. Combination $\infty P . oP . [\infty P\infty] . -P . -2P\infty . +2P\infty . +4P\infty$.

The crystals have a specific gravity of 1·554 (Schiff), and a cooling saline, somewhat ammoniacal taste; they dissolve easily in water, the solution giving off part of its ammonia on evaporation. They effloresce on the surface when exposed to the air, and at a gentle heat give off their water and a portion of their ammonia. At a stronger heat the salt melts with strong intumescence, giving off all its water and ammonia, and leaving pure metaphosphate of sodium, which in the fused state easily dissolves metallic oxides, forming di- and tri-metallic phosphates, possessing in many cases very characteristic colours. On account of these reactions, the salt is much used as a flux in blowpipe experiments.

Uelsmann (Arch. Pharm. [2] xcix. 138; Jahresb. 1859, p. 75), in preparing sodio-ammonic phosphate, once obtained it in long efflorescent prisms containing $Na(NH^4)HPO^4.5H^2O$, but on dissolving them in water containing ammonia, and recrystallising, ordinary microcosmic salt with 4 at. water was obtained.

*Sodio-diammonic phosphate*, $Na(NH^4)^2PO^4.4H^2O$, separates in dazzling white pearly crystalline laminæ on adding strong ammonia to a cold saturated aqueous solution of microcosmic salt. On exposure to the air, it gives off ammonia and is converted into ordinary microcosmic salt, which also crystallises out when a solution of the diammonic salt is left to evaporate spontaneously. On one occasion the diammonic salt crystallised with 5 at. water. A solution of the diammonic salt in hot saturated aqueous ammonia yielded less lustrous crystals of a salt containing $(NH^4)^3PO^4.Na(NH^4)^2PO^4.6H^2O$. (Uelsmann.)

*Sodio-barytic Orthophosphate*, $NaBa''PO^4$.—Prepared by igniting 1 at. dibarytic orthophosphate with 1 at. carbonate of sodium; but it is decomposed in great part by washing with water, the residue always containing a considerable quantity of tribarytic phosphate. (H. Rose.)

*Sodio-lithic Orthophosphate*, $(Li; Na)^3PO^4$.—This double salt, which contains variable proportions of sodium and lithium, the two metals replacing one another isomorphously, is obtained by mixing a solution of ordinary phosphate of sodium with a lithium-salt, evaporating to dryness, and treating the residue with water, the double salt, which is very slightly soluble, then remaining behind. It forms a white light powder like phosphate of calcium or magnesium, requiring nearly 1400 pts. of water at 15°, 1233 pts. at 60°, and 950 pts. at 100°, to dissolve it; in water containing phosphate of sodium it is almost insoluble. According to **Rammelsberg**, this salt generally contains from 9·9 to 15·3 per cent. lithium (22 to 34 per cent. lithia); but according to **Fresenius** the salt obtained by evaporating the solution of a lithium-salt with phosphate of sodium, adding a quantity of soda sufficient to keep the liquid alkaline, and digesting the residue with aqueous ammonia, is pure trilithic phosphate, $Li^3PO^4$, containing 18·9 per cent. lithium. (See LITHIUM, iii. 728.)

*Sodio-magnesic phosphate*, $NaMg''PO^4$, is obtained, mixed with a large quantity of trimagnesic phosphate, by igniting dimagnesic phosphate with an equivalent quantity of sodic carbonate and washing out the soluble salts with water.

*Sodio-manganoso-ferric phosphate*, $(Na^2; Mn'')^3PO^4.Fe'''PO^4.\frac{1}{2}H^2O$, is said to occur as a clove-brown mineral at Limoges. (Handw. d. Chem. vi. 374.)

*Sodio-potassic orthophosphate*, $NaKHPO^4.8H^2O$, is obtained by neutralising a solution of monosodic orthophosphate with carbonate of potassium or the monopotassic salt with carbonate of sodium, and evaporating. It then separates completely in monoclinic crystals, in which $a : b : c = 0·8144 : 1 : 1·1056$. Angle of inclined axes = 83° 39′; $\infty P : \infty P$ (orthod.) = 101° 20′; $\infty P2 : \infty P2$ (orthod.) = 62° 46; $+P\infty : c$ = 44° 58; $oP : \infty P$ = 85° 59′. The crystals are usually tabular, from predominance of $oP$, but exhibit also the faces $\infty P$, $\infty P\infty$, $[\infty P\infty]$. $+P$, $-P$. $+P\infty$. The salt is easily soluble in water, gives off its water of crystallisation when moderately heated, and the basic water on ignition.

γ. *Pyrophosphates of Sodium.*—The *disodic* or *acid salt*, $Na^2H^2P^2O^7$, is formed by heating disodic orthophosphate with strong hydrochloric acid to 150°—160°, or by exposing monosodic orthophosphate, $NaH^2PO^4.H^2O$, to a heat of about 200°; also by dissolving tetrasodic pyrophosphate in acetic acid and adding alcohol, whereupon it separates as a white crystalline powder. Larger crystals may be obtained by carefully pouring alcohol on the concentrated aqueous solution of the salt, so that the two liquids may not mix, and leaving the whole at rest. The salt is easily soluble in water, and remains on evaporation as a friable crust (**Schwarzenberg**). When heated for some time to 220°, it loses half its basic hydrogen. (**Fleitmann** and **Henneberg**.)

The *tetrasodic* or *neutral pyrophosphate*, $Na^4P^2O^7.10H^2O$, is obtained by igniting disodic orthophosphate, and may be crystallised by solution in water and evaporation. The crystals are monoclinic prisms, permanent in the air, easily soluble in water, but less soluble than the disodic orthophosphate. The solution has an alkaline reaction, and the salt contained in it is not converted into orthophosphate by boiling *per se*, even for several days, but the conversion takes place easily on addition of nitric, hydrochloric, or even acetic acid. The crystallised salt gives off all its water of crystallisation when gently heated in the air, or in a vacuum at ordinary temperatures, but the dehydrated salt when exposed to the air gradually takes up again the same amount of water. The dry salt melts at a high temperature, and solidifies on cooling to a colourless, opaque, vitreous mass.

Tetrasodic pyrophosphate, being easily prepared in considerable quantity, is much used for the preparation of insoluble pyrophosphates and soluble double pyrophosphates.

*Sodio-aluminic pyrophosphate.*—The precipitate formed by sodic pyrophosphate in solutions of aluminium dissolves easily in excess of the sodium-salt (being thereby distinguished from orthophosphate of aluminium), and the solution when evaporated becomes turbid at a certain concentration, depositing part of the aluminic pyrophosphate, whilst a salt richer in alkali remains in solution, and is not precipitated either by ammonia or by sulphide of ammonium.

*Sodio-ammonic pyrophosphate*, $Na^2(NH^4)^2P^2O^7.5H^2O$, is obtained by evaporating a solution of monosodic pyrophosphate saturated with ammonia over a mixture of sal-ammoniac and quicklime. It forms white monoclinic prisms easily soluble in water; on boiling the solution, ammonia is given off and disodic pyrophosphate remains. (**Schwarzenberg**.)

*Sodio-antimonic pyrophosphate.*—Monosodic pyrophosphate, boiled with recently precipitated antimonious oxide, dissolves a portion of it, and the filtrate yields by evaporation a cauliflower-like mass, which is decomposed by water, the greater part of the antimonious oxide then remaining undissolved.

*Sodio-auric pyrophosphate*, $2Na^4P^2O^7.Au'''^4P^6O^{21}.H^2O$.—Trichloride of gold dissolves in aqueous sodic pyrophosphate, and if the solution, which is colourless after warming, be evaporated in a vessel in which it is protected from light and dust, chloride of sodium and the excess of sodic pyrophosphate separate out, and the double salt remains as a syrupy solution, having, according to Persoz, the above composition. The solution has been used for galvanic gilding.

*Sodio-barytic pyrophosphate*, $Na^4P^2O^7.6Ba''^2P^2O^7.6H^2O$.—This is said to be the composition of a double salt produced as an amorphous precipitate, on dropping chloride of barium into a boiling solution of sodic pyrophosphate.

*Sodio-bismuth-pyrophosphate.*—Monosodic pyrophosphate dissolves a rather large quantity of bismuth-oxide. Also when bismuth-nitrate is washed with excess of solution of sodic pyrophosphate, a soluble double salt is formed, whose solution becomes turbid when heated, but, according to Persoz, is not precipitated by sulphide of ammonium.

*Sodio-calcic pyrophosphate,* $Na^2Ca''P^2O^7.4H^2O$ (Baer).—This salt separates when a solution of chloride of calcium is dropt into excess of sodic pyrophosphate.

*Sodio-chromic pyrophosphate.*—Known only in solution, which resembles that of the potassio-chromic salt (p. 576).

*Sodio-cobaltous pyrophosphate.*—The precipitate formed by sodic pyrophosphate in the solution of a cobaltous salt dissolves in excess of the former; the solution turns blue when heated, and the cobalt is precipitated by sulphide of ammonium.

*Sodio-cupric pyrophosphates.*—When a solution of sodic pyrophosphate is boiled with excess of recently precipitated cupric pyrophosphate, the hot filtered liquid deposits a white crystalline insoluble crust, consisting, after drying at 100°, of $Na^4\overset{''}{Cu}{}^4P^8O^{28}.7H^2O$. The supernatant liquid slowly evaporated over the water-bath yields a faintly bluish crystalline crust, also insoluble in water, and consisting of $3Na^2Cu''P^2O^7.2H^2O$ (at 100°). The mother-liquor decanted therefrom and left to evaporate spontaneously, deposits first the excess of sodic pyrophosphate, then splendid blue crystals of the salt $Na^6Cu''P^4O^{14}.2H^2O$ (at 100°). Each of these three double salts melts at a red heat (Fleitmann and Henneberg). Persoz, by a method not exactly described, obtained the double salts $Na^2Cu''P^2O^7.6H^2O$ and $Na^6Cu''P^4O^{14}.6H^2O$, which are the same as the second and third of those above described, but with larger quantities of water, Persoz having analysed them in the air-dried state.

*Sodio-ferric pyrophosphate,* $Na^8\overset{'''}{Fe}{}^4P^{10}O^{35}.7H^2O$ or $2Na^4P^2O^7.\overset{'''}{Fe}{}^4P^6O^{21}: 7H^2O$, separates in the pure state when ferric pyrophosphate, after being washed with a quantity of sodic pyrophosphate not sufficient to dissolve it, is heated and the filtrate mixed with alcohol (Fleitmann and Henneberg). The same salt is obtained in solution when pyrophosphate of sodium is added to a ferric solution till the precipitate at first formed is redissolved. The double salt is white and very soluble in water. The solution is colourless, and does not taste like iron-salts in general. Ammonia colours it blood-red, but does not render it turbid; sulphydric acid colours it brown without forming a precipitate; sulphide of ammonium precipitates sulphide of iron from it immediately according to H. Rose, gradually according to Persoz. The solution evaporated to a syrup soon deposits ferric pyrophosphate.

*Sodio-ferrous pyrophosphate* is known only in solution, as obtained by mixing a ferrous salt with excess of sodic pyrophosphate. It oxidises quickly on exposure to the air, and the iron is completely precipitated from it by sulphide of ammonium.

*Sodio-magnesic pyrophosphate* is an amorphous precipitate formed on dropping sulphate of magnesium into a boiling solution of sodic pyrophosphate. (Baer.)

*Sodio-ammonio-manganous pyrophosphate,* $Na(NH^4)Mn''P^2O^7.3H^2O$ according to Otto, $Na^4(NH^4)^4\overset{''}{Mn}{}^2P^6O^{21}.12H^2O$ according to Berzelius, is formed, on pouring a solution of manganous chloride mixed with ammonia and sal-ammoniac into a warm solution of sodic pyrophosphate, as a white amorphous precipitate which soon becomes crystalline. When somewhat strongly heated, it gives off all its ammonia and leaves a semifused mass having an acid reaction. (Otto.)

*Sodio-plumbic pyrophosphate,* $Na^2Pb''P^2O^7$.—White granular insoluble precipitate, formed by adding sodic pyrophosphate to nitrate of lead, and boiling the resulting precipitate with excess of the sodium-salt (Gerhardt). The salt formed on slowly adding nitrate of lead to excess of sodic pyrophosphate till the precipitate becomes permanent, also contains sodium but in variable quantity.

*Sodio-potassic pyrophosphate,* $Na^2K^2P^2O^7.12H^2O$, is obtained by saturating monosodic pyrophosphate with potassic carbonate. The solution evaporated to a syrup solidifies on cooling to a pasty mass, consisting of transparent, slender needles, having the form of an oblique rhombic prism. The salt dissolves easily in water, forming an alkaline solution. (Schwarzenberg.)

δ. Respecting Fleitmann and Henneberg's phosphates of sodium, $Na^6P^4O^{13}$ or $Na^3PO^4.3NaPO^3$ and $Na^{12}P^{10}O^{31} = Na^3PO^4.9NaPO^3$, see pp. 537, 538.

**Phosphates of Strontium.** α. *Metaphosphate.*—The salt prepared by dissolving carbonate of strontium in phosphoric acid, and heating the evaporated residue to 316°, is a white powder, insoluble in water and in dilute acids, decomposed by strong sulphuric acid.

β. *Orthophosphates.*—The *di-strontic salt,* $\overset{''}{Sr}{}^2H^2P^2O^8$, obtained by precipitation, is a white, amorphous, tasteless powder, insoluble in pure water, but soluble in water containing ammoniacal salts or free acids; not decomposed by aqueous alkalis. When heated before the blowpipe it melts to a white enamel, exhibiting phosphorescence. A solution of chloride of strontium incompletely precipitated in the cold with an alkaline phosphate yields, according to Kühn, a mixture of distrontic and monostrontic salt.

*Strontio-potassic orthophosphate*, $Sr''KPO^4$, and *strontio-sodic orthophosphate*, $Sr''NaPO^4$, are formed, according to Rose, by ignition 1 at. pyrophosphate of strontium with 1 at. carbonate of potassium or sodium, and washing out the mass with water; but the double salts are for the most part decomposed by the water, the residue always containing neutral phosphate of strontium.

γ. *Pyrophosphate*, $\overset{\prime\prime}{Sr}{}^2P^2O^7.H^2O$ (at 100°).—Obtained by precipitation as a white, amorphous powder, which gradually becomes crystalline when warmed in the liquid. It is nearly insoluble in water, quite insoluble in acetic acid, but easily soluble in the stronger acids. It gives off its water when heated above 100° (Schwarzenberg). The precipitate formed on gradually adding nitrate of strontium to a boiling solution of sodic pyrophosphate, appears to be a mixture of the pure strontium-salt with a double salt. (Baer.)

**Phosphato-tantalic Acid.** A solution of tantalic acid in sulphuric or hydrochloric acid yields, with strong aqueous phosphoric acid, a white, opaque jelly. Tantalic oxide heated with phosphoric oxide forms a colourless glass.

**Phosphate of Tellurium** is a white powder, insoluble in water. (Berzelius.)

**Phosphate of Thallium.** A hot solution of nitrate of thallium, mixed with excess of phosphoric acid and then with ammonia, forms a crystalline precipitate, probably consisting of *trithallic phosphate*, $Tl^3PO^4$, inasmuch as, when boiled with nitrate of silver, it yields yellow phosphate of silver, without rendering the solution acid. 1 pt. of this salt dissolves in 201·2 pts. of water at 15° and in 149 pts. at 100°. It is sparingly soluble in acetic acid, but dissolves easily in nitric acid. When heated it melts to a brown liquid, which becomes orange-yellow on cooling, and finally solidifies to a white crystalline mass (Crookes, Chem. Soc. J. xvii. 135; Chem. News, ix. 37). Lamé (Jahresb. 1862, p. 186), who probably obtained an acid phosphate of thallium, states that it is soluble in water and crystallises from a dilute solution.

**Phosphate of Thorinum.** Flocculent precipitate, forming a white powder when dry, insoluble in water and in phosphoric acid, melting with difficulty before the blowpipe. (Berzelius.)

**Phosphates of Tin.** *Stannic oxide* forms with excess of phosphoric acid a salt containing $2SnO^2.P^2O^5.10H^2O$ (Haeffely, Phil. Mag. [4] x. 290). Stannic phosphate is insoluble in nitric acid, a property on which is founded Reynoso's method of separating phosphoric acid from bases (p. 544).

*Stannous phosphate*, $3SnO.P^2O^5$ or $\overset{\prime\prime}{Sn}{}^3P^2O^8$, according to Kühn, is formed on mixing stannous chloride with ordinary phosphate of sodium, as a white precipitate, insoluble in water after drying, but easily soluble in mineral acids, and melting to a vitreous mass before the blowpipe. According to Lenssen (Ann. Ch. Pharm. cxiv. 113; Jahresb. 1860, p. 183), the composition of the precipitate varies with the proportion in which the solutions are mixed. When a solution of disodic orthophosphate acidulated with acetic acid is added to a large excess of concentrated solution of stannous chloride, a precipitate is formed containing, when air-dried, $\overset{\prime\prime}{Sn}{}^3P^2O^8.Sn''Cl^2.2H^2O$, and not decomposed by hot water; but when the phosphate of sodium is in excess, the air-dried precipitate contains $\overset{\prime\prime}{Sn}{}^3P^2O^8.\overset{\prime\prime}{Sn}{}^2H^2P^2O^8.3H^2O$. This salt remains unaltered at 100°, but is decomposed at a red heat, yielding metallic tin, stannic oxide, and phosphoric acid.

**Phosphate of Titanium.** Tetrachloride of titanium forms with phosphoric acid a white, bulky, flocculent precipitate, which dries up to a gummy shining mass, insoluble in water, but soluble in excess either of phosphoric acid or of titanic chloride.

**Phosphates of Uranium.** α. *Uranic Orthophosphates.*—The composition of these phosphates, as of other uranic salts, is most easily represented by regarding them as containing the diatomic radicle uranyl, $U^2O^2$. (See URANIUM.)

The *monouranylic salt*, $(U^2O^2)''H^4P^2O^8.3H^2O$, is obtained by digesting uranic oxide with phosphoric acid and boiling the mass with water. The yellow liquid thus obtained yields, by evaporation over sulphuric acid, lemon-yellow crystals, which give off part of their water at a gentle heat, becoming dull and light-yellow; the rest of the water goes off at a red heat, and the remaining dry salt does not melt even when very strongly heated. Water, especially if hot, abstracts part of the phosphoric acid.

The *di-uranylic salt*, $(\overset{''}{U}{}^2O^2)^2H^2P^2O^8$, is obtained in combination with various quantities of water according to the mode of preparation adopted. When uranic oxide is digested with a sufficient quantity of phosphoric acid, and the product washed with water, a tri-hydrate, $(U^2O^2)^2H^2P^2O^8.3H^2O$, remains as a light yellow amorphous powder, which gives off its water of crystallisation between 120° and 170°, and the basic water at a red heat, leaving the pyrophosphate $(U^2O^2)^2P^2O^7$. A hexhydrate, $(U^2O^2)^2H^2P^2O^8.6H^2O$, is obtained by precipitating uranic nitrate with ordinary phosphate of sodium. The precipitate, after washing and drying, is a light yellow slightly crystalline powder, which gives off its water of crystallisation at 120°, the basic water at a red heat. The octohydrate, $(U^2O^2)^2H^2P^2O^8.8H^2O$, is obtained by adding phosphoric acid to uranic acetate as long as a precipitate forms. This precipitate, when washed, is crystalline, and somewhat darker-coloured than the trihydrate. It gives off 2 at. water at 60°, and then exhibits all the properties of the hexhydrate.

The *tri-uranylic salt*, or *neutral uranic phosphate*, $3U^2O^3.P^2O^5$ or $(\overset{''}{U}{}^2O^2)^3P^2O^8$, has not been obtained in the pure state. The light yellow precipitate formed on mixing uranic nitrate with an equivalent quantity of trisodic phosphate appears to consist of $5U^2O^3.H^2O.2P^2O^5$ + aq. or $(U^2O^2)^3P^2O^8.(U^2O^2)^2H^2P^2O^8.H^2O$. When a larger quantity of trisodic phosphate is added, but not sufficient to redissolve the precipitate, a double salt is formed containing $\left.\begin{matrix}5U^2O^3\\Na^2O\end{matrix}\right\}2P^2O^5.3H^2O$ or $(U^2O^2)^3P^2O^8.(U^2O^2)^2Na^2P^2O^8.3H^2O$. This salt is a dark yellow coherent powder, insoluble in water, decomposed by acetic acid, which dissolves out soda and uranic oxide. (**Werther**, Ann. Ch. Pharm. lxviii. 312.)

*Calcio-uranic Phosphate*, $\left.\begin{matrix}2U^2O^3\\Ca''O\end{matrix}\right\}P^2O^5.8H^2O$ or $(\overset{''}{U}{}^2O^2)^2Ca''P^2O^8.8H^2O$.—This compound occurs native as uranite (also called *lime uranite* and *uranium mica*) in dimetric crystals, having the principal axis = 2·115; P : P (terminal) = 95°, 46′; P : P (basal) = 143° 2′. Ordinary combination, oP . P . ∞P, the face oP being mostly predominant, and giving the crystals a tabular form. Cleavage perfect parallel to oP. Hardness = 2 to 2·5. Specific gravity = 3·05 to 3·19. Colour citron to sulphur-yellow. Lustre of oP pearly, of other faces subadamantine. Transparent to subtranslucent. Fracture not observable. Sectile. Laminæ brittle and not flexible. Before the blowpipe it melts to a blackish semi-crystalline mass. Dissolves with yellow colour in nitric acid.

The first of the following analyses is of uranite from Autun by **Berzelius** (Pogg. Ann. i. 374); the second by **Werther** (*loc. cit.*).

| $P^2O^5$ | $U^2O^3$ | $Ca''O$ | $Ba''O$ | $Mg''O$ and $Mn''O$ | $H^2O$ | $SnO^2$ | | |
|---|---|---|---|---|---|---|---|---|
| 15·20 | 61·73 | 5·88 | 1·57 | 0·20 | 15·48 | 0·06 | = | 100·12 |
| 14·00 | 63·28 | 5·88 | 1·03 | . . | 14·30 | . . | = | 98·47 |

The formula above given requires 15·55 $P^2O^5$, 62·56 $U^2O^3$, 6·13 $Ca''O$, and 15·76 water.

Uranite occurs in the Siebengebirge; at Johangeorgenstadt and Eibenstock in Saxony; on Wolf Island, Lake Onega, Russia; near Limoges and at St. Symphorien near Antun; also at Chesterfield, Massachusetts; Ackworth, New Hampshire; and on the Schnykell near Philadelphia.

*Cuprico-uranic Phosphate*, $\left.\begin{matrix}2U^2O^3\\Cu''O\end{matrix}\right\}P^2O^5.8H^2O$ or $(\overset{''}{U}{}^2O^2)^2Cu''P^2O^8.8H^2O$.—This compound occurs native as chalcolite (also called *copper-uranite* and *turberite*), a mineral isomorphous with uranite. Hardness = 2·25. Specific gravity 3·5 to 3·6. Colour emerald and other shades of green. Streak somewhat paler. The other physical properties are like those of uranite. Before the blowpipe it melts to a black mass, colouring the flame bluish-green. Gives with borax a green glass, sometimes becoming reddish-brown in the reduction-flame. Dissolves in nitric acid with yellowish-green colour.

Analyses of chalcolite from Cornwall:

| $P^2O^5$ | $U^2O^3$ | $Cu''O$ | $H^2O$ | | | |
|---|---|---|---|---|---|---|
| 15·57 | 81·39 | 8·44 | 15·05 | = | 100·45 | Berzelins. |
| 14·34 | 59·03 | 8·27 | 15·39 | = | 97·03 | Werther. |

The formula requires 15·16 $P^2O^5$, 61·00 $U^2O^3$, 8·48 $Cu''O$, and 15·36 water.

Chalcolite is found at Gunnis Lake near Callington, also near Redruth, and elsewhere in Cornwall; at Johangeorgenstadt, Eibenstock, and Schneeberg in Saxony; at Joachimsthal and Zinnwald in Bohemia; and at Vielsalm in Belgium.

**Debray** (Jahresb. 1860, p. 73) has obtained crystals having the form and composition of chalcolite, by mixing a solution of acid cupric phosphate with uranic nitrate.

β. *Uranous Orthophosphate*, $U''HPO_4.H_2O$.—Ordinary phosphate of sodium added by drops to uranous chloride forms a green gelatinous precipitate, insoluble in water. When recently precipitated it dissolves in strong hydrochloric acid, and is separated therefrom by water; after drying it no longer dissolves in acids. Ammonia has scarcely any action upon it; melting potash withdraws almost all the phosphoric oxide.

γ. *Uranic Pyrophosphate* is granular when recently precipitated, but cakes together if left on the filter for a few days, forming a very friable mass with conchoïdal fracture.

*Sodio-uranic Pyrophosphate.*—Precipitated uranic pyrophosphate dissolves in excess of sodic pyrophosphate, forming a yellow solution, which yields no crystals even when evaporated to a syrup; the uranium is not precipitated from it either by sulphydric acid or by sulphide of ammonium.

**Phosphates of Vanadium.** Vanadic dioxide dissolves in aqueous phosphoric acid, forming a blue solution, which when evaporated at temperatures below 50° yields small blue deliquescent crystals, easily soluble in water, insoluble in alcohol. When heated they give off water, leaving a loose spongy mass resembling burnt alum, and caking together at a white heat to a black substance no longer soluble in water.

*Phosphato-vanadic acid.*—Vanadic anhydride (trioxide) dissolves in aqueous phosphoric acid, forming a red solution, which when evaporated leaves a red deliquescent saline mass. Vanadic phosphate heated with a sufficient quantity of nitric acid forms a red solution, which deposits on evaporation a lemon-yellow crystalline crust, soluble with yellow colour in water. The crystals when heated give off water and turn light yellow. A solution of vanadic phosphate and sodic phosphate in nitric acid becomes colourless when evaporated, and deposits yellow crystalline grains which dissolve slowly in water, forming a yellow solution which dries up on evaporation to a yellow varnish-like mass.

A compound of phosphoric, vanadic, and silicic anhydrides containing, according to Berzelius, $3SiO_2.2VaO_3.2P_2O_5.6H_2O$, was obtained from the refinery slag of the Taberg iron works. It may be produced by dissolving silicate, vanadate, and phosphate of sodium in nitric acid, evaporating to a pulp, and washing with cold water. It then remains in nacreous scales, which when heated give off water and acquire a straw-yellow colour. It is easily soluble in water, whence it crystallises unaltered on evaporation. The solution is coloured green by nitric peroxide and other reducing agents, and yields with carbonate of ammonium a precipitate of gelatinous silica.

**Phosphate of Yttrium.** $Y''_3P_2O_8.5H_2O = 3Y''O.P_2O_5.5H_2O$.—Disodic orthophosphate added to the solution of an yttrium-salt throws down an amorphous precipitate, which by prolonged washing with water is resolved into a soluble acid salt, and an insoluble neutral salt having the composition just given. (**Popp**, Jahresb. xvii. 204.)

Tri-yttric phosphate likewise occurs, together with cerous phosphate, as **xenotime**, in dimetric crystals P . ∞P, having the principal axis = 0·6201; angle P : P (terminal) = 124° 26′; P : P (basal) = 82° 30′. Cleavage perfect, parallel to ∞P. Hardness = 4 to 5. Specific gravity = 4·39 to 4·55. Lustre resinous. Colour yellowish brown to flesh-red. Streak paler. Opaque. Fracture uneven and splintery. It is infusible before the blowpipe; with borax it slowly forms a clear glass, which, with a larger quantity of the mineral, becomes turbid on cooling; in microcosmic salt it dissolves very slowly. It is insoluble even in strong acids.

*Analyses.*—*a.* From the Flekkefjord in Norway: specific gravity 4·557 (**Berzelius**, Pogg. Ann. iii. 203).—*b.* From the same locality; specific gravity 4·45 (**Zschaw**, *Rammelsberg's Mineralchemie*, p. 321).—*c.* From the gold-washings at Clarksville, Georgia: specific gravity = 4·54 (**Smith**, Sill. Am. J. xviii. 377):

| | $P_2O_5$ | $Y''O$ | $Ce''O$ | $Fe_2O_3$ | $SiO_2$ | | |
|---|---|---|---|---|---|---|---|
| *a.* | 33·49* | 62·58 | . . | 3·93 | . . | = | 100 |
| *b.* | 30·74 | 60·25 | 7·98 | . . | . . | = | 98·97 |
| *c.* | 32·45 | 54·13 | 11·03† | 2·06 | 0·89 | = | 100·56 |

*Castelnaudite*, occurring in crystals (apparently dimetric) and grains, in the diamond sand of Bahia, consists mainly of phosphate of yttrium. **Damour** (Institut. xxi. 78) found in a sample having a specific gravity of 4·39, 31·64 per cent. $P_2O_5$, 60·40 yttria, 7·4 titanic oxide and zirconia, 1·2 uranic and ferric oxides.

* With trace of fluorine.

† With lanthanum and didymium.

**Phosphates of Zinc.** *α. Metaphosphates.*—When a zinc-salt is treated with phosphoric acid in the same manner as for the preparation of cupric di-metaphosphate (p. 560), the mass on slow cooling yields indistinct crystals of zinc-dimetaphosphate, $\overset{\prime\prime}{Zn}{}^2P^4O^{12}$. It is insoluble in water, and is not decomposed by dilute aqueous acids or alkalis, or by sulphide of ammonium. When treated with strong ~~sulphuric acid~~ or fused with an alkaline carbonate, it yields orthophosphoric acid.

A mixture of aqueous zinc-chloride and ammonium-dimetaphosphate yields the hydrated salt $Zn^2P^4O^{12}.8H^2O$ in small transparent crystals, insoluble in water, but decomposed by boiling therewith. The water of crystallisation is not completely expelled below a red heat, and the salt does not melt even at a bright red heat. The constitution of the salt does not appear to be altered by heating. (Fleitmann.)

*β. Orthophosphates.*—The *monozincic* or *acid phosphate* is formed by dissolving zinc, or the carbonate or phosphate of zinc in excess of phosphoric acid and evaporating. It is a gummy mass which melts in the fire to a transparent glass. When a small quantity of alkali is added to its aqueous solution, the neutral salt is deposited. (Wenzel.)

The *dizincic salt*, $\left.\begin{matrix}2Zn''O\\H^2O\end{matrix}\right\}P^2O^5.2H^2O$ or $\overset{\prime\prime}{Zn}{}^2H^2P^2O^8.2H^2O$, is deposited in shining laminæ on mixing a solution of 3 pts. of zinc-sulphate in 32 pts. of hot water, with a solution of 4 pts. of crystallised disodic orthophosphate in 32 pts. of hot water. The crystals do not lose water at 100°; but at a temperature below the melting point of tin they give off 2 at. water, retaining their lustre; at a red heat the dehydrated salt fuses and gives off its basic water. (Graham.)

The *trizincic* or *neutral salt*, $3ZnO.P^2O^5.2H^2O$ or $\overset{\prime\prime}{Zn}{}^3P^2O^8.2H^2O$, is precipitated on mixing a solution of a zinc-salt with disodic orthophosphate, the supernatant liquid becoming acid. When the solutions are dilute and mixed in the cold, a translucent jelly is at first produced; this, however, soon becomes opaque, and aggregates into a fine white crystalline powder. If the solutions are mixed boiling hot, no jelly is produced, but the pulverulent precipitate is formed at once and has the same composition. The same compound is doubtless formed on digesting carbonate of zinc with aqueous phosphoric acid not in excess. It is a white, crystalline, tasteless powder which melts easily, forming a transparent and colourless glass. It is insoluble in water, soluble in acids, likewise in ammonia and in carbonate, sulphate, chloride and nitrate of ammonium—in the last three, however, with slight turbidity.

The same salt with 6 at. water separates in large flat prisms and laminæ when a solution of the acid zinc-salt is mixed with absolute alcohol. (Reynoso.)

*Phosphate of Zinc and Ammonium.*—When a solution of sulphate or chloride of zinc is precipitated with phosphate of ammonium containing free ammonia, a white, bulky, flocculent precipitate is formed which, when digested in the liquid, becomes crystalline after the free ammonia has escaped. The dry salt is a white powder, insoluble in water, but soluble in acids and in free potash, soda, or ammonia. Its composition appears to be intermediate between $Zn^2(NH^4)^2P^2O^8.2H^2O$ and $Zn^2(NH^4)^2P^2O^8.Zn''H^2O^2.2H^2O$. (Bette, Ann. Ch. Pharm. xv. 129.)

*γ. Pyrophosphate of Zinc* is formed by precipitating a zinc-salt with pyrophosphate of sodium. The precipitate is decomposed by boiling with ordinary phosphate of sodium, yielding ordinary orthophosphate of zinc and pyrophosphate of sodium (Stromeyer). The salt precipitated as above forms a white bulky mass, which in drying shrinks up like hydrate of aluminium. If it be suspended in water, and sulphurous acid gas passed through the liquid, the whole dissolves, and the solution, when boiled, yields the salt in the form of a heavy, white, beautifully crystalline powder consisting of $2Zn^2P^2O^7.3H^2O$. Both the amorphous and the crystalline salt dissolve in acids and in caustic potash; ammonia likewise dissolves the salt, and alcohol added to the solution throws down a syrupy mass. (Schwarzenberg.)

*Zinco-ammonic pyrophosphate* is obtained as a white pulverulent precipitate, on adding pyrophosphate of sodium to a solution of zinc-chloride mixed with ammonia and sal-ammoniac. (Bette.)

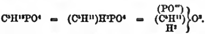
**Phosphate of Zirconium**, $3ZrO^2.P^2O^5$ or $(Zr''O)^3P^2O^8$, is precipitated on mixing a soluble zirconium-salt with free phosphoric acid or an alkaline phosphate; in the former case part of the salt remains in solution, but may be precipitated on addition of ammonia. The precipitate is a gummy, translucent mass, like hydrate of aluminium, remaining translucent when dry. It is insoluble in water, somewhat soluble in free phosphoric acid.

### *Alcoholic Phosphates: Phosphoric Ethers.*

Each of the three hydrogen-atoms in orthophosphoric acid may be replaced by alcohol radicles, giving rise to acid and neutral ethers analogous to the metallic phosphates. There are also several sulphophosphoric ethers, having the composition of orthophosphoric ethers, in which the oxygen is more or less replaced by sulphur. A neutral pyrophosphate of ethyl is also known, but no metaphosphoric ethers have yet been obtained. In connection with these alcoholic phosphates may also be mentioned an acid consisting of phosphoric acid in which the hydrogen is partly replaced by acetyl.

**Phosphates of Amyl** or **Amyl-phosphoric Ethers.** Two of these compounds are known, viz. mono- and di-amylphosphoric acid; the neutral ether has not been obtained.

1. *Amylphosphoric acid,*



$$C^5H^{13}PO^4 = (C^5H^{11})H^2PO^4 = \left.\begin{matrix}(PO''') \\ (C^5H^{11}) \\ H^2\end{matrix}\right\}O^3.$$

(Guthrie, Chem. Soc. Qu. J. ix. 134.)—This ether is prepared by mixing equal weights of syrupy phosphoric acid and amylic alcohol, leaving the mixture in a warm place for a day, neutralising with carbonate of potassium, evaporating over the water-bath to dryness, dissolving in strong alcohol, and evaporating repeatedly (whereby the potassium-salt is obtained), then precipitating by acetate of lead, filtering and washing (whereby the lead-salt is obtained), precipitating the lead by sulphydric acid, then filtering, and evaporating in vacuo.

It is a colourless, transparent, crystalline, deliquescent mass, easily soluble in water and in alcohol, but insoluble in ether. It bears the heat of a water-bath without decomposition. When heated in the flame of a lamp it burns with a white flame, leaving a residue of phosphoric acid. It is a strong acid, and decomposes carbonates.

The amylphosphates, $C^5H^{11}M^2PO^4$, are all anhydrous at 100°: those of the alkali-metals are soluble in water; the rest are insoluble or sparingly soluble, and may be prepared from the potassium-salt by double decomposition. They all dissolve readily in nitric or hydrochloric acid, and bear the heat of the water-bath without decomposition.

The *potassium-salt*, $C^5H^{11}K^2PO^4$, prepared as above, is tenacious, finely crystalline, translucent, and deliquescent; yields amyl-alcohol when heated in a tube. A solution of this salt subjected to electrolysis yields at the positive pole, carbonic anhydride and oxygen, and an acid liquid smelling of valeric or butyric acid, while the liquid at the negative pole gives off hydrogen, but remains odourless, showing that no amyl-compound is there eliminated.

The *ammonium-salt*, $C^5H^{11}(NH^4)^2PO^4$, obtained by direct neutralisation, or by decomposing the copper- or lead-salt with sulphide of ammonium, resembles the potassium-salt.

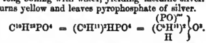
The *barium-salt*, $C^5H^{11}Ba''PO^4$, is precipitated in white scales having a silky lustre.

The *lead-salt*, $C^5H^{11}Pb''PO^4$, dried at 100°, is a bulky white anhydrous powder.

The *copper-salt*, $C^5H^{11}Cu''PO^4$, is almost white when first precipitated, but gradually turns bluish, and in the dry state forms a light blue amorphous powder.

The *silver-salt*, $C^5H^{11}Ag^2PO^4$, is a white bulky precipitate, which turns grey on exposure to light, and is decomposed by long boiling with water, yielding metallic silver. When heated on platinum-foil, it turns yellow and leaves pyrophosphate of silver.

2. *Diamyl-phosphoric acid,*



$$C^{10}H^{23}PO^4 = (C^5H^{11})^2HPO^4 = \left.\begin{matrix}(PO)''' \\ (C^5H^{11})^2 \\ H\end{matrix}\right\}O^3.$$

(Fehling, Handw. d. Chem. i. 793.)—This compound is prepared by adding 1 pt. pentachloride of phosphorus very gradually to 1½ or 2 pts. of amylic alcohol, rise of temperature being checked. The product is heated in a retort to expel the simultaneously formed chloride of amyl and hydrochloric acid, then thrown into water saturated with carbonate of sodium, and shaken with ether; the ethereal solution of amylic alcohol is removed, and the diamyl-phosphoric acid isolated by adding hydrochloric acid. The acid so formed contains two additional atoms of water, which are removed by drying over sulphuric acid in vacuo.

Diamylphosphoric acid is an oily liquid of specific gravity 1·025 at 20°, but floating in hot water. It is nearly inodorous, but has a strong acid taste. It is nearly insoluble in water, but dissolves easily in alcohol and ether. It is permanent at ordinary temperatures, but decomposes when distilled, yielding amylic alcohol. When boiled with water it also yields amylic alcohol, and the residual liquid probably contains mono-amylphosphoric acid.

Diamylphosphoric acid is a strong acid, and saturates bases completely. The **diamylphosphates**, $(C^5H^{11})^2MPO^4$ and $(C^5H^{11})^4M''P^2O^8$, are all anhydrous, and are decomposed by boiling with water, giving off amyl-alcohol, and apparently being converted into mono-amylphosphates. The di-amylphosphates of the alkali-metals are very soluble in water, and remain as uncrystallisable unctuous masses when their solutions are evaporated; those of the alkaline earth-metals are but slightly soluble in water, more soluble in alcohol. The aqueous solutions give precipitates with plumbic, cupric, manganous, mercurous salts, &c. The following salts have been examined by Marx and Lemppenau.

The *barium-salt*, $(C^5H^{11})^4Ba''P^2O^8$, obtained by digesting the aqueous acid with carbonate of barium, and evaporating in vacuo or at a gentle heat, forms silky, asbestos-like masses of crystals.—The *calcium-salt*, prepared in like manner, is also crystalline. —The *copper-salt* is a greenish-blue precipitate, soft and unctuous when dried.—The *ferric salt*, $(C^5H^{11})^6Fe'''P^3O^{12}$, obtained by precipitation, is a whitish powder, insoluble in water and in alcohol.—The *lead-salt*, $(C^5H^{11})^4Pb''P^2O^8$, obtained by precipitating the ammonium-salt with acetate of lead, is a loosely coherent, curdy precipitate, insoluble in water and in alcohol. By precipitating with excess of lead-acetate, a dense pulverulent precipitate is formed consisting of a basic salt, $(C^5H^{11})^4Pb''P^2O^8.Pb''H^2O^2$. —The *mercurous salt* obtained by precipitation appears to decompose in drying, and then forms a grey powder.

*Ethylic diamylphosphate*, $(C^2H^5)(C^5H^{11})^2PO^4$, appears to be formed—1. By heating a solution of diamylphosphoric acid in 3 or 4 pts. alcohol of 95 per cent. in a sealed tube to 180°; on treating the contents of the tube with aqueous carbonate of sodium, a mobile liquid separates, having an ethereal odour.—2. By heating diamylphosphate of silver with iodide of ethyl to 100°.

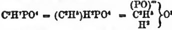
*Triamylic Phosphate* or *Neutral Phosphate of Amyl*, $(C^5H^{11})^3PO^4$, has not been obtained pure, but appears to be formed by heating diargentic amylphosphate with chloride of amyl to 180° in a sealed tube:

$$C^5H^{11}Ag^2PO^4 + 2C^5H^{11}Cl = 2AgCl + (C^5H^{11})^3PO^4.$$

On treating the product with alcohol and mixing the decanted solution with water, an ethereal liquid separates, having an odour quite different from that of amylic alcohol. (Guthrie.)

**Ethylic Phosphates. Ethylphosphoric Ethers.** Four of these compounds are known, namely, the three orthophosphates of ethyl and the neutral pyrophosphate; also several sulphophosphates.

ETHYLPHOSPHORIC ACID, also called *Phosphethylic* or *Phosphovinic acid*,



$$C^2H^7PO^4 = (C^2H^5)H^2PO^4 = \left.\begin{matrix}(PO)'''\\ C^2H^5\\ H^2\end{matrix}\right\}O^3.$$

—This compound was discovered by Lassaigne in 1820 (Ann. Ch. Phys. [2] xiii. 294), and has been further examined by Pelouze (*ibid.*, lii. 37), Liebig (Ann. Ch. Pharm. vi. 149), and Church (Proc. Roy. Soc. xiii. 520). It is produced by the action of phosphoric acid on alcohol or ether, the latter reaction being however slower than the former; also by the action of phosphoric oxychloride on aqueous alcohol. (Schiff.)

*Preparation.*—1 pt. of 95 per cent. alcohol is mixed with 1 pt. of syrupy orthophosphoric or pyrophosphoric acid, the mixture heated for some minutes to 60° or 80°, diluted after 24 hours with eight times its bulk of water, and neutralised with finely pulverised carbonate of barium. The whole is boiled for a while to drive off the uncombined alcohol, then left to cool down to 70°, filtered, and the filtrate left in a cold place that the ethylphosphate of barium may crystallise out. From the aqueous solution of this salt the acid may be obtained by carefully adding sulphuric acid and filtering; it may also be obtained by decomposing the lead-salt with sulphydric acid and filtering. Either of these filtrates evaporated, first over the open fire, and then over oil of vitriol in vacuo at ordinary temperatures, leaves the concentrated acid in the form of an oil, which neither dries up nor decomposes when left for a longer time in vacuo. (Pelouse.)

The concentrated acid is a colourless, inodorous, viscid oil, which reddens litmus strongly, and has a biting sour taste. It deposits a few shining crystals of the acid, which, however, do not increase at 22°. When boiled, it first gives off ether mixed with alcohol, then ethylene gas with a trace of wine-oil, and leaves phosphoric acid mixed with charcoal (Pelouse). When distilled with acetate of potassium, it yields pure acetic ether. (Liebig, Ann. Ch. Pharm. xiii. 32.)

The acid mixes with water in all proportions, and may be concentrated by boiling up to a certain point without decomposition (Pelouse). It likewise mixes in all proportions with alcohol and ether.

**Ethylphosphates**, $C^2H^5M^2PO^4$.—These salts are all more or less soluble in water and crystallisable. The lead-salt is the least soluble. Most of them have a maximum degree of solubility at about 40—60°.

The *ammonium-salt* is easily prepared by saturating the acid with ammonia. The aqueous solution becomes acid on evaporation, but the salt may be obtained in a semi-crystalline form by evaporation in vacuo over oil of vitriol. When carefully heated in an oil-bath it gives off ammonia as well as water, but appears to yield ethylphosphamic acid, among other products.

*Arsenious ethylphosphate*, $(C^2H^5)^3\overset{'''}{As}{}^2P^3O^{12}$, is obtained in beautiful feathery crystals by dissolving arsenious anhydride in the boiling aqueous acid and evaporating; also by warming a mixture of arsenious chloride and an equivalent quantity of anhydrous ethylphosphate of lead (or silver), exhausting the mass with warm water, and evaporating the filtrate. This latter method, however, is not so good as the former, as the salt is slowly decomposed by water into arsenious anhydride and ethylphosphoric acid. (Church.)

*Ethylphosphate of Barium*, $(C^2H^5)Ba''PO^4.6H^2O$, prepared as above, forms colourless, very short, right rhombic prisms, passing into six-sided tables by truncation of the acute lateral edges. It tastes agreeably saline and bitter, effloresces very slowly in the air, gives off its water of crystallisation at 120°, acquiring at the same time a pearly lustre. The crystals of the hexhydrated salt immersed in a boiling saturated solution immediately assume a pearly aspect, and are found after drying in vacuo to be converted into the monohydrate, $(C^2H^5)Ba''PO^4.H^2O$. On the other hand, this monohydrate, or the anhydrous salt, when treated with cold water, is immediately reconverted into the hexhydrate. A saturated solution of the ordinary salt evaporated at 50°—60° deposits pearly plates of a hydrate intermediate between the mono- and hexhydrates, viz. $(C^2H^5)^2Ba^2P^2O^8.7H^2O$. (Church.)

The anhydrous salt heated to dull redness gives off water and carburetted hydrogen with traces of alcohol and ether, and leaves dibarytic pyrophosphate mixed with charcoal. The principal decomposition is represented by the equation:

$$2C^2H^5Ba''O^4 \;=\; \overset{''}{Ba}{}^2P^2O^7 + 2C^2H^4 + H^2O.$$

If the dry salt be mixed, before ignition, with carbonate of potassium, it likewise yields no alcohol, but the same volatile products as when heated alone (Pelouze). From the cold aqueous solution mixed with nitric acid, alcohol throws down nitrate of barium, leaving ethylphosphoric acid in solution.

The salt is most soluble in water at 40°, and the solution saturated at that temperature deposits crystals of the 6-hydrated salt, both when heated and when cooled; 1 pt. of the (hexhydrated?) salt dissolves in 29·4 pts. water at 0°, in 30·3 pts. at 5°, in 14·9 pts. at 20°, in 10·7 pts. at 40°, in 12·5 pts. at 50°, in 11·2 pts. at 55°, in 12·4 pts. at 60°, in 22·3 pts. at 80°, and 35·7 pts. at 100°. The salt is insoluble in alcohol and ether, and is precipitated by those liquids from its aqueous solution.

The aqueous solution precipitates the salts of lead, mercury, and silver, but not those of iron, nickel, copper, gold, or platinum.

The *calcium-salt* forms micaceous scales slightly soluble in pure water.

*Ferric ethylphosphate*, $(C^2H^5)^6\overset{''''}{Fe}{}^4P^6O^{24}.6H^2O$, is obtained by precipitating a hot solution of the silver-salt, with an equivalent quantity of ferric chloride also dissolved in hot water, and separates in straw-yellow films from the filtrate when heated to the boiling-point. (Church.)

By precipitating mixtures of ferric and aluminic chlorides in various proportions with ethylphosphate of silver, or heating mixed solutions of ferric and aluminic ethylphosphates to the boiling-point, or adding absolute alcohol to them till only a part is precipitated, Church has obtained *ferrico-aluminic ethylphosphates* containing respectively $(C^2H^5)^6\overset{'''}{Fe}{}^3Al'''P^6O^{24}.6H^2O$, $(C^2H^5)^6\overset{'''}{Fe}{}^2Al^2P^6O^{24}.6H^2O$, and $(C^2H^5)^6Fe'''Al^3P^6O^{24}.6H^2O$.

A *ferroso-ferric ethylphosphate*, $(C^2H^5)^6\overset{''}{Fe}{}^3\overset{'''}{Fe}{}^2P^6O^{24}.6H^2O$, is obtained by precipitating the barium-salt with a solution of mixed ferrous and ferric sulphates, and adding alcohol to the filtrate.

The *lead-salt*, $(C^2H^5)Pb''PO^4.H^2O$, obtained by precipitating a solution of the barium-salt nearly saturated at 70° with acetate of lead, is almost insoluble in cold water, but slightly soluble in hot water, from which it may be crystallised. It may be obtained anhydrous by heating it to 130°—150°. (Church.)

A *mercurous salt*, apparently containing $(C^2H^5)Hg^2PO^4.2H^2O$, is obtained by precipitation from moderately concentrated solutions in pearly plates. It dissolves slightly and with partial decomposition in cold water, but is insoluble in alcohol. (Church.)

The *potassium-* and *sodium-salts*, obtained by precipitating the barium-salt with the corresponding sulphates, are deliquescent and difficult to crystallise.

The *silver-salt*, $(C^2H^5)Ag^2PO^4.H^2O$, is crystalline and sparingly soluble.

The *strontium-salt* crystallises with difficulty in hydrated crystals, is much less soluble in hot than in cold water, and is precipitated from the cold aqueous solution by alcohol.

The *uranic salt*, $(C^2H^5)(U^2O^2)''PO^4.H^2O$, is obtained by dissolving uranic oxide in ethylphosphoric acid, and evaporating the filtered solution in pale yellow flocks, which dry up to amorphous, brittle, lemon-yellow masses. It is less soluble in boiling water than in water at 60° or 70°.

*Ethylphosphate of Tetrethylammonium*, $(C^2H^5)(C^8H^{20}N)^2PO^4$, is obtained by precipitating a hot solution of the silver-salt with iodide of tetrethylammonium, and evaporating the filtrate, first at 100°, then over sulphuric acid in vacuo. It forms a confused mass of crystals, which lose their transparency on drying, are extremely soluble in cold water, and deliquescent. It begins to decompose at 100°, and is completely resolved at higher temperatures into triethylamine and triethylic phosphate:

$$(C^2H^5)[(C^2H^5)^4N]^2PO^4 \;=\; 2(C^2H^5)^3N \;+\; (C^2H^5)^3PO^4.$$

**ETHYL-SULPHOPHOSPHORIC ACID**, $C^2H^7PSO^3 = C^2H^5.H^2.PSO^3$.—This acid, discovered by Cloez (Compt. rend. xxiv. 388), is known only in aqueous solution, and in its salts. The *potassium-* and *sodium-salts* are easily obtained by agitating sulphochloride of phosphorus with alcoholic potash or soda:

$$C^2H^6O \;+\; 5KHO \;+\; PSCl^3 \;=\; C^2H^5K^2PSO^3 \;+\; 3KCl \;+\; 3H^2O.$$

They dissolve readily in water and in alcohol.

The *barium-*, *strontium-*, and *calcium-salts*, obtained by saturating the aqueous acid with the corresponding carbonates, are crystallisable. The formula of the barium-salt is $C^2H^5Ba''PSO^3$.

**DIETHYL-PHOSPHORIC ACID**, $C^4H^{11}PO^4 \;=\; (C^2H^5)^2HPO^4 \;=\; \left.\begin{matrix}(PO)'''\\(C^2H^5)^2\\H\end{matrix}\right\}O.$

(Vögeli, Ann. Ch. Pharm. lxix. 180.)—This acid is formed, together with the preceding, when absolute alcohol or ether, in the liquid or gaseous state, is brought in contact with phosphoric anhydride. The absorption of the vapour affords the best mode of preparation, because when phosphoric anhydride is introduced into liquid alcohol or ether, great heat is evolved, and the phosphoric anhydride forms into lumps, which are very slowly acted upon.

*Preparation.*—Phosphoric anhydride is placed over anhydrous ether or alcohol (the latter yields the best product), and the whole is covered with a bell-jar to keep out the moisture of the air. The anhydride then absorbs the vapour, and in a week or a fortnight deliquesces to a syrup. This syrup is saturated with carbonate of lead, the insoluble phosphate of lead, &c., removed by filtration, and the filtrate evaporated over a water-bath or a sand-bath. A sparingly soluble lead-salt (ethylphosphate) then separates out in pearly crystals. On further concentration, the solution yields groups of crystals like caffeine. These crystals consist of the diethylphosphate of lead; they may be purified by redissolving them at a very gentle heat and recrystallising. From the solution of this lead-salt the lead may be precipitated by sulphydric acid; and the filtrate evaporated in vacuo yields the hydrated acid in the form of a syrup, which does not crystallise, and appears to be partially decomposed.

The syrupy acid when heated gives off pungent acid vapours, and afterwards phosphoric ether, recognisable by its odour. The decomposition terminates with a violent frothing of the whole mass, and phosphoric acid remains behind.

The *diethylphosphates* have the composition $(C^2H^5)^2MPO^4$ or $(C^2H^5)^4M''P^2O^8$, according to the atomicity of the metal. They appear to be all soluble in water.

The *barium-salt* is formed by saturating the aqueous acid with carbonate of barium. It dissolves readily in water and dilute alcohol, and may be obtained in needles and laminæ.

The *calcium-salt*, $(C^2H^5)^4Ca''P^2O^8$, is obtained by adding carbonate or hydrate of calcium to phosphoric anhydride which has been left to deliquesce over alcohol or ether, or to the aqueous acid prepared by decomposing the lead-salt with sulphydric acid, or by decomposing the lead-salt with an alcoholic solution of chloride of calcium.

It is very soluble in water, less soluble in dilute alcohol, sparingly in absolute alcohol, crystallises on cooling from a warm, concentrated aqueous solution, or from an aqueous solution gradually evaporated, in silky groups of crystals like the lead-salt, From the solution in dilute alcohol it crystallises in needles. When strongly heated, it does not give off water or fuse, but decomposes, with evolution of triethylic phosphate, turning slightly black at the same time.

The *copper-salt*, obtained by decomposing the lead-salt with sulphate of copper, is very soluble in water.

The *lead-salt*, $(C^2H^5)^4Pb''P^2O^8$, prepared as above, dissolves readily in cold water, still more in warm water, and separates on cooling from a warm concentrated solution in groups of crystals resembling caffeine. It is sparingly soluble in cold, easily in hot absolute alcohol. It melts at 180°, solidifying to a crystalline mass on cooling. When heated to about 190° it is resolved into triethylic phosphate, which distils over, and ethylphosphate of lead:

$$(C^2H^5)^4Pb''P^2O^8 \;=\; (C^2H^5)^3PO^4 \;+\; (C^2H^5)Pb''PO^4.$$

The other diethylphosphates are decomposed by heat in a similar manner.

The *magnesium-* and *nickel-salts* are very soluble in water; the latter crystallises in groups of laminæ.

**Diethylsulphophosphoric acid**, $(C^2H^5)^2HPSO^3$. (**Carius**, Ann. Ch. Pharm. cxii. 190; Jahresb. 1859, p. 442.)—This acid is formed, together with triethylic disulphophosphate, by the action of pentasulphide of phosphorus on alcohol:

$$5C^2H^6O \;+\; P^2S^5 \;=\; (C^2H^5)^2HPSO^3 \;+\; (C^2H^5)^3PS^2O^2 \;+\; 2H^2S.$$

Diethylsulphophosphoric acid is a viscid, oily liquid having a strongly acid and likewise bitter taste. It may be boiled in aqueous or alcoholic solution without decomposition, but decomposes when strongly heated *per se*, giving off mercaptan (and perhaps also sulphide of ethyl), and leaves phosphoric acid. It forms very stable salts, among which the *ammonium-*, *potassium-*, *sodium-*, *barium-*, *calcium-*, and *lead-salts* dissolve easily in water, and are soluble also in absolute alcohol and even in ether; the *silver-salt* is nearly insoluble in water, but very soluble in alcohol and in ether. The silver-, lead-, and zinc-salts separate from their solutions by rapid evaporation in oily drops, which remain viscid for a long time, but solidify in the crystalline form when touched with a hard body.

**Diethyl-disulphophosphoric acid**, $(C^2H^5)^2HPS^2O^2$ (**Carins**, *loc. cit.*).—Produced, together with ethylic sulphide, by heating triethylic disulphophosphate (*infra*) with mercaptan in a sealed tube:

$$\underset{\substack{\text{Triethylic disul-}\\\text{phophosphate.}}}{(C^2H^5)^3PS^2O^2} \;+\; \underset{\substack{\text{Mercap-}\\\text{tan.}}}{C^2H^5.H.S} \;=\; \underset{\substack{\text{Diethyl-disul-}\\\text{phosphoric}\\\text{acid.}}}{(C^2H^5)^2HPS^2O^2} \;+\; \underset{\substack{\text{Ethylic}\\\text{sulphide.}}}{(C^2H^5)^2S.}$$

It is a transparent, colourless, amorphous mass, viscid at a gentle heat. Its salts are produced by the action of alcoholic sulphydrate of potassium or sodium on triethylic disulphophosphate, mercaptan being formed at the same time:

$$(C^2H^5)^3PS^2O^2 \;+\; KHS \;=\; (C^2H^5)^2KPS^2O^2 \;+\; C^2H^5.H.S.$$

**Diethyl-tetrasulphophosphoric acid**, $(C^2H^5)^2HPS^4$.—The potassium-salt of this acid is formed by the action of alcoholic sulphydrate of potassium on triethylic tetrasulphophosphate. (**Carius**, *loc. cit.*)

**Triethylic Phosphate**, $(C^2H^5)^3PO^4 = \left.\begin{matrix}(PO)''' \\ (C^2H^5)^3\end{matrix}\right\}O^3$.—This ether was discovered by **Vögeli**, who obtained it—1. By heating diethylphosphate of lead to 190° (*vid. sup.*).—2. In small quantity, together with diethylphosphoric acid, by the action of phosphoric anhydride on alcohol. It is likewise produced—3. By heating phosphate of silver with iodide of ethyl to 100° (a slight action takes place also at common temperatures), exhausting the mass with ether, heating the liquid which remains after the evaporation of the ether to 160°, and distilling it in vacuo at 140° (**De Clermont**, Ann. Ch. Pharm. xci. 376).—4. By the action of oxychloride of phosphorus on ethylate of sodium:

$$3C^2H^5NaO \;+\; POCl^3 \;=\; 3NaCl \;+\; (C^2H^5)^3PO^4.$$

The liquid filtered from the chloride of sodium is freed from ether by heating it in the water-bath, and the residue is distilled (**Limpricht**, Ann. Ch. Pharm. cxxxiv. 347).—5. By the action of the oxychloride on absolute alcohol. (**Schiff.**)

Triethylic phosphate is a limpid liquid, having a peculiar odour, a specific gravity of 1·072 at 12°, and boiling at 215°. It is soluble in water, alcohol, and ether, but is slowly decomposed by contact with water. (**Carius.**)

**Triethylic Disulphophosphate**, $(C^2H^5)^3PS^2O^2$, is obtained, together with diethylsulphophosphoric acid (*vid. sup.*), by the action of pentasulphide of phosphorus on alcohol. It is a colourless oily liquid, having an aromatic and somewhat alliaceous odour, especially when warmed, and distilling undecomposed with vapour of water.

When treated with alcoholic sulphydrate of potassium or sodium, it yields diethyl-disulphophosphoric acid and mercaptan (Carius, p. 592). With *alcohols*, it yields diethyl-sulphophosphoric acid, together with a sulphide of ethyl, and the radicle of the alcohol employed; *e.g.* with amylic alcohol:

$$(C^2H^5)^2PS^2O^2 + (C^5H^{11})HO = (C^2H^5)^2HPS^2O^3 + (C^2H^5)(C^5H^{11})S.$$

TRIETHYLIC TETRASULPHOPHOSPHATE, $(C^2H^5)^3PS^4$. (Carius, *loc. cit.*)—Produced by the action of pentasulphide of phosphorus on mercaptan, or better, on mercaptide of mercury:

$$3(C^2H^5)^2Hg''S^2 + P^2S^5 = 2(C^2H^5)^3PS^4 + 3Hg''S.$$

It is a light yellow oily liquid resembling triethylic disulphophosphate, but more easily decomposible. With alcoholic sulphydrate of potassium it yields diethyl-tetrasulphophosphoric acid, and with hydrate of potassium, the potassium-salt of another acid, probably diethyl-trisulphophosphoric acid, $(C^2H^5)^2HPS^3O$.

TETRETHYLIC PYROPHOSPHATE, $(C^2H^5)^4P^2O^7$. (De Clermont, *loc. cit.*)—Produced by heating dry pyrophosphate of silver with iodide of ethyl to 100° in a sealed flask. The filtered liquid is then distilled at the heat of the water-bath, and the viscid residue is dried by passing air through it at 130°, and then heating it in vacuo to 140°. It is a viscid liquid, of specific gravity 1·172 at 17°; has a peculiar odour and burning taste; burns with a whitish flame, diffusing white vapours. Potash decomposes it, forming crystallisable deliquescent diethylphosphate of potassium. It is soluble in water, alcohol, and ether, soon turns acid when exposed to the air, and dissolves a small quantity of silver-iodide.

**Methylic Phosphates** or **Methylphosphoric ethers.** The monomethylic and dimethylic phosphates have been obtained by Hugo Schiff (Ann. Ch. Pharm. cii. 334); the trimethylic ether is not known.

The two acid ethers are produced simultaneously: 1. By the action of phosphoric oxychloride on methylic alcohol:

$$3(CH^3)HO + POCl^3 = (CH^3)H^2PO^4 + 2CH^3Cl + HCl,$$

and

$$3(CH^3)HO + POCl^3 = (CH^3)^2HPO^4 + CH^3Cl + 2HCl.$$

On mixing the two liquids, great heat is evolved, vapours of hydrochloric acid and chloride of methyl given off, and a dark red liquid remains consisting of mono- and dimethylphosphoric acids, the former being in the greater quantity. But, if the phosphoric oxychloride be placed in a flask attached to the lower end of a condensing apparatus, and standing in cold water, and the wood-spirit be added by drops from the upper end, each addition being made only after the reaction produced by the former has subsided, the product consists almost entirely of dimethylphosphoric acid, which, after the red liquid has been freed from hydrochloric acid and wood-spirit by heating it for several hours in the water-bath, remains in the form of a colourless syrup, but by continued heating over the water-bath is gradually resolved into wood-spirit and phosphoric acid.

2. By the action of pentachloride of phosphorus on methylic alcohol, phosphoric oxychloride being first formed, as shown by the equation,

$$(CH^3)HO + PCl^5 = POCl^3 + CH^3Cl + HCl,$$

and then acting on the rest of the methylic alcohol as above.

*Dimethylphosphoric acid*, $(CH^3)^2HPO^4 = \left.\begin{matrix}(PO)''' \\ (CH^3)^2 \\ H\end{matrix}\right\}O^3$, is very sour, attacks zinc with evolution of hydrogen, and decomposes carbonates with facility. The aqueous solution is readily decomposed by boiling, apparently with formation of monomethylphosphoric acid. It is soluble in alcohol and ether.

The dimethylphosphates, $(CH^3)^2MPO^4$ and $(CH^3)^4M''P^2O^8$, are obtained by neutralising the aqueous acid with the corresponding carbonates. Some of the less soluble may also be obtained by precipitation. They are easily separated from the monomethylphosphates, which are much less soluble and separate out on evaporation. The dimethylphosphates are mostly colourless, dissolve pretty readily in water, less in alcohol, not at all in ether, and are precipitated by alcohol and ether from their concentrated solutions.—Almost all of them contain several atoms of water of crystallisation.—Their aqueous solutions are decomposed by evaporation, unless the heat is kept very low. By distillation they yield the same products as the free acid, with a residue of phosphate.

The *barium-salt*, $(CH^3)^4Ba''PO^4$, forms nacreous laminæ nearly insoluble in alcohol. The *strontium-salt*, $(CH^3)^4Sr''P^2O^8.2H^2O$, is somewhat more soluble in alcohol than the barium-salt, and crystallises from the alcoholic solution by gradual evaporation in silky crystalline laminæ arranged in radiated groups. It gives off its water at 160°.—

The *calcium-salt*, $(CH^3)^4Ca''P^2O^8$, separates in warty masses, very soluble in water.—The *magnesium-salt* is a white powder soluble in water.—The *zinc-salt* is white and rather soluble.—The *iron* and *copper-salts* appear also to be easily soluble, inasmuch as the solution of the salt is not precipitated by solutions of iron, calcium, or copper.—The *lead-salt*, $(CH^3)^4Pb''P^2O^8$, is precipitated from the concentrated aqueous solution by ether in flakes.

The soluble dimethylphosphates form white precipitates with salts of *cobalt*, *mercury*, and *silver*.

The monomethylphosphates, $(CH^3)M^2PO^4$, are much less soluble in water than the dimethylophosphates. The *barium-salt*, $(CH^3)Ba''PO^4.2H^2O$, is less soluble in water at 100° than in lukewarm water, and separates as soon as the solution is placed over the water-bath, in laminæ having a strong lustre. It gives off the greater part of its water of crystallisation even on exposure to the air, a further portion over sulphuric acid, losing its lustre at the same time, and the whole (2 at.) at 150°. When strongly heated it gives off combustible gases.

*Sulphochloride of phosphorus* forms with methylic alcohol an acid ether, whose barium-salt is soluble in water. This ether is probably monomethylic sulphophosphoric acid, $(CH^3)H^2PSO^3$.

Addendum. *Methylphosphorous acid*, $CH^5PO^3 = \left.\begin{matrix}P'''\\ CH^3\\ H^2\end{matrix}\right\}O^3$ (Schiff, *loc. cit.*).—Produced by the action of trichloride of phosphorus on methylic alcohol:

$$3CH^4O + PCl^3 = CH^5PO^3 + 2CH^3Cl + HCl.$$

Trichloride of phosphorus is added by drops to methylic alcohol as long as any action takes place, and the liquid is left in a warm place for several hours, to expel hydrochloric acid and excess of methylic alcohol. The compound is thus obtained in the form of a nearly colourless, very acid syrup, which draws out into threads, and cannot be made to crystallise. On attempting to concentrate it further by heat, it is resolved into methylic alcohol and phosphorous acid.

The *methylphosphites*, $(CH^3)HMPO^3$, are obtained by treating the corresponding carbonates with the aqueous acid. By evaporation at ordinary temperatures or at a very gentle heat, they are obtained as amorphous masses which exhibit crystalline structure when scratched with a sharp-edged tool. When strongly heated, they give off phosphoretted hydrogen and combustible hydrocarbons, leaving a residue of phosphate mixed with a little amorphous phosphorus. They are hygroscopic, and dissolve readily in water, sparingly in alcohol, and not at all in ether. The aqueous solutions decompose slowly at ordinary temperatures into methylic alcohol and phosphates. This decomposition takes place most quickly when the solutions are acid, and may be prevented by keeping an excess of the carbonate in the liquid during evaporation.

The *barium-salt*, $(CH^3)^2H^2Ba''P^2O^6$, is anhydrous, less soluble in water and in alcohol than the calcium-salt. The *calcium-salt*, $(CH^3)^2H^2Ca''P^2O^6.2H^2O$, gives off its water at 100°. The *lead-salt*, $(CH^3)^2H^2Pb''P^2O^6$, is very easily decomposed by heat.

The solution of the calcium-salt does not precipitate the chlorides of copper and iron; with *mercuric chloride*, it forms a white precipitate; and with *nitrate of silver*, a precipitate which is white at first but quickly yields reduced silver.

**Phenylic Phosphates** or **Phenylphosphoric Ethers.**—1. *Monophenylphosphoric acid*, $(C^6H^5)H^2PO^4$, has been obtained by Church (Proc. Roy. Soc. xiii. 520), but the mode of preparation is not described. Both the acid and its salts oxidise rapidly.

2. *Diphenylphosphoric acid*, $C^{12}H^{11}PO^4 = \left.\begin{matrix}(PO)'''\\ (C^6H^5)^2\\ H\end{matrix}\right\}O^3$.—This acid ether is obtained by the action of pentachloride of phosphorus on phenylic alcohol prepared from salicylic acid (p. 390), and appears to constitute the chief portion of the product. At ordinary temperatures it is a granular crystalline powder, and after being freed from adhering liquid by pressure between paper, may be kept in paper in the warmest and dampest weather without alteration. It dissolves easily in a weak solution of caustic soda to which a little alcohol is added, forming the *diphenylphosphate of sodium*, $(C^6H^5)^2NaPO^4$, which crystallises on cooling from a hot saturated solution in prisms or needles. These crystals yield by analysis 22·64, 22·82, and 22·91 per cent. water, and 8·96, 8·91, and 9·02 per cent. phosphorus, agreeing nearly with the formula, $2(C^6H^5)^2NaPO^4.9H^2O$, which requires 22·95 per cent. water and 8·78 per cent. phosphorus. Sometimes (under circumstances not precisely determined) flattened needles were obtained containing 24·56—24·81 per cent. water; the formula $(C^6H^5)^2NaPO^4.5H^2O$ requires 24·81 per cent. On mixing the aqueous solution of the sodium-salt with neutral acetate of lead, a nacreous crystalline precipitate is formed containing 29·2

per cent. lead, which agrees nearly with the formula $(C^6H^5)^4Pb''P^2O^8$, requiring 29·4 per cent. (H. Watts, *Gmelin's Handbook*, xii. 249; and *unpublished experiments.*)

Hugo Müller, in making some experiments with the view of obtaining phenylene from phenol by the action of phosphoric anhydride, has recently obtained a phenylphosphoric acid, the formula of which is however not yet made out. When phosphoric anhydride is brought in contact with crystalline phenol, elevation of temperature takes place and a pasty mass is formed, which on heat being applied becomes homogeneous. The temperature being raised still higher, unchanged phenol distils over, but there is no indication that phenylene is formed in this reaction. On dissolving the residuary mass in water and treating it with barium-carbonate, a solution of phenylphosphate of barium is obtained, which, after precipitation of the barium-salt with sulphuric acid and careful evaporation, yields the phenylphosphoric acid in the state of a heavy oily liquid, which separates from the concentrated solution. This phenyl-phosphoric acid forms with most metals well crystallised salts.—The *potassium-*, *sodium-* and *ammonium-salts* are very readily soluble in water.—The *magnesium-salt* crystallises with difficulty, and is moderately soluble in water.—The *barium-salt* crystallises in magnificent asbestos-like crystals. Solutions of the barium-salt give with acetate of lead a white flocculent precipitate, which soon becomes converted into a mass of fibrous crystals. Dilute solutions give no precipitate, but on evaporation yield crystals resembling the barium-salt.—The *silver-salt* is a white precipitate which soon becomes yellow and brown. Solutions of the phenyl-phosphate of barium do not give precipitates with *copper-*, *cobalt-*, *nickel-*, *or zinc-salts* in the cold, but when heat is applied, precipitates are formed which dissolve again on cooling. The phenylphosphates like the corresponding ethylphosphates possess the peculiar property of being less soluble in hot water than in cold: their maximum solubility appears to lie between 40° and 60°. (*Communication from Dr. Müller.*)

***Triphenylic Phosphate,*** $(C^6H^5)^3PO^4 = \left.\begin{matrix}(PO)'''\\(C^6H^5)^3\end{matrix}\right\}O^3$. (Williamson and Scrugham, Chem. Soc. Qu. J. vii. 240.)—This compound, the neutral phosphate of phenyl, is produced, together with chloride of phenyl, by the action of pentachloride of phosphorus on phenylic alcohol obtained from coal-tar creosote, and constitutes that portion of the product (the largest) which distils above the range of the mercurial thermometer. It is purified by treating the crude product with strong aqueous potash, removing the potash by washing with water, and distilling the remaining liquid two or three times.

This ether, at the ordinary temperatures, is a thick, oily, fluorescent liquid, but solidifies at low temperatures to a mass of crystals. It is inodorous, soluble in alcohol and ether, but insoluble in potash except on boiling. It is very expansible, sinking in a cold solution of potash, but rising to the surface on the application of heat, and again falling to the bottom on cooling. It is decomposed by ethylate of sodium, or by evaporation to dryness with strong potash; and on adding nitrate of potassium to the residue, fusing, treating the fused mass with water, and neutralising with hydrochloric acid, a solution is obtained in which the phosphoric acid may be detected and estimated in the usual way with ammonia and sulphate of magnesium. The ether gave by analysis, 65·92 per cent. carbon, 5·13 hydrogen, and 8·00 phosphorus, the formula $(C^6H^5)^3PO^4$ requiring 66·11 carbon, 4·59 hydrogen, 9·7 phosphorus and 19·59 oxygen.

**Glycerophosphoric Acid,** $C^3H^9PO^6 = \left.\begin{matrix}(PO)'''\\(C^3H^5)'''\\H^4\end{matrix}\right\}O^6$, existing in the yolk of eggs and in the brain, and produced artificially by the action of phosphoric acid or anhydride on glycerin, has been already described (ii. 896).

**Acetylphosphoric Acid,** probably $C^4H^9PO^7 = \left.\begin{matrix}(PO)'''\\(C^2H^3O)^2\\H\end{matrix}\right\}O^3.H^2O$, is obtained by the action of acetylic chloride on phosphate of silver. On treating the resulting mass with water, the acetylphosphoric acid dissolves, together with phosphoric acid; and by neutralising the evaporated filtrate with carbonate and hydrate of calcium, precipitating with acetate of lead, and decomposing the lead-salt with sulphydric acid, the acetylphosphoric acid is obtained as a viscid liquid which is resolved by boiling the solution into phosphoric and acetic acids. The *barium-* and *calcium-salts* are easily soluble; the former, $C^4H^5Ca''PO^6.4H^2O$, crystallises in radiate needles and prisms permanent in the air. (Kämmerer and Cairns, Ann. Ch. Pharm. cxxxi. 170.)

**Acetylpyrophosphoric Acid,** $(C^2H^3O)H^3P^2O^7 = \left.\begin{matrix}(P^2O^3)^{iv}\\C^2H^3O\\H^3\end{matrix}\right\}O^4$. (N. Menschutkine, Bull. Soc. Chim. 1865, i. 269.)—Produced by the action of nitric acid, or better of hydric peroxide on acetylpyrophosphorous acid, $(C^2H^3O)H^3P^2O^5$ (p. 534).—

The *barium-salt*, $(C^2H^3O)HBa''P^2O^7.2H^2O$, is obtained by adding a solution of barium-peroxide in dilute hydrochloric acid to a solution of potassic acetylpyrophosphite. It is a crystalline precipitate, insoluble in water, moderately soluble in dilute acids. Its solution in nitric acid, decomposed by an equivalent quantity of sulphuric acid, yields the aqueous acid; and on neutralising this with ammonia, and adding acetate of lead, the *lead-salt*, $(C^2H^3O)^2\bar{Pb}^3P^4O^{14}$, is obtained as a precipitate, insoluble in water, easily soluble in dilute nitric acid.—The *silver-salt*, $(C^2H^3O)Ag^3P^2O^7$, obtained in like manner, is a white precipitate which gradually turns yellowish. It dissolves without decomposition in dilute nitric acid and in dilute ammonia, but strong ammonia poured on the dry salt reduces part of the silver.

Acetylpyrophosphoric acid is slowly converted into phosphoric acid by ebullition with aqueous acid and alkalis, quickly by fusion with hydrate of potassium or carbonate of sodium.

**PHOSPHORUS, OXYBROMIDE OF.** $POBr^3$.—This compound, discovered by Gladstone (Phil. Mag. [3] xxxv. 345; Jahresb. 1849, p. 243), is produced by the decomposition of the pentabromide in moist air: $PBr^5 + H^2O = 2HBr + POBr^3$; and in a pure state by the action of the pentabromide on alcohols and acids, *e.g.*, by treating 1 at. of the strongest acetic acid with 1 at. of the pentabromide (H. Ritter, Ann. Ch. Pharm. xiv. 210):

$$\underset{\text{Acetic acid.}}{C^2H^3O.H.O} + PBr^5 = \underset{\text{Oxybromide of phosphorus.}}{POBr^3} + \underset{\text{Bromide of acetyl.}}{C^2H^3OBr} + HBr;$$

or 1 at. fused oxalic acid with 1 at. pentabromide (Baudrimont, Bull. Soc. Chim. 1861, p. 118), the reaction being similar to that with the pentachloride (*infra*). After rectification, it forms a crystalline mass composed of large laminæ, melts at 45° or 46° to a colourless liquid; has a specific gravity of 2·822 [solid or liquid?]; boils at 195° (Ritter). It is slowly decomposed by water into phosphoric and hydrobromic acids, and acts upon alcohols, acids, &c. in the same manner as the oxychloride.

**PHOSPHORUS, OXYCHLORIDE OF.** $POCl^3$.—This compound, discovered by Wnrtz (Ann. Ch. Phys. [3] xx. 472), is produced by reactions analogous to those above described for the formation of the oxybromide. Gerhardt (Ann. Ch. Phys. [3] xxxvii. 285) recommends, as the best mode of preparing it, to distil pentachloride of phosphorus with half its weight of oxalic acid completely deprived of its water of crystallisation:

$$C^2H^2O^4 + PCl^5 = POCl^3 + 2HCl + CO + CO^2;$$

or 5 pts. of the pentachloride with 1 pt. or rather more of crystallised boric acid (*ibid.* xlv. 102):

$$2H^3BO^3 + 3PCl^5 = 3POCl^3 + B^2O^3 + 6HCl.$$

In either case, hydrochloric acid is given off as gas, and oxychloride of phosphorus is the only liquid product of the distillation. The oxychloride is also produced by passing oxygen gas into boiling trichloride of phosphorus; and by mixing the pentachloride with phosphoric anhydride: $P^2O^5 + 3PCl^5 = 5POCl^3$; and according to Lnutemann (p. 535) by heating phosphoric anhydride with dry chloride of sodium.

Oxychloride of phosphorus is a colourless fuming liquid having a specific gravity of 1·7 and boiling at 110°. It is decomposed by water like the oxybromide, yielding hydrochloric and phosphoric acids:

$$POCl^3 + 3H^2O = 3HCl + H^3PO^4.$$

Like pentachloride of phosphorus, the oxychloride is largely used for preparing the chlorides of different radicles, according to a reaction first introduced by Gerhardt (*loc. cit.*); with *acetate of potassium* for example it yields phosphate of potassium and chloride of acetyl:

$$3(C^2H^3O.K.O) + POCl^3 = K^3PO^4 + 3C^2H^3OCl$$

(see Chlorides, i. 897). Heated with *metallic oxides*, it forms a metallic chloride and phosphate. Heated to 100° in a sealed tube with *oxychloride of chromium*, it reacts in the manner shown by the equation:

$$10POCl^3 + 12CrO^2Cl^2 = 3Cr^2O^3 + 6CrCl^3 + 5P^2O^5 + 18Cl^2. \quad \text{(Caseelman.)}$$

With *aqueous alcohol* of ordinary strength it forms monoethylphosphoric acid, and with *anhydrous alcohol*, triethylic phosphate (Schiff, Jnhresb. 1857, p. 10):

$$POCl^3 + C^2H^5.H.O + 2H^2O = C^2H^5.H^2.PO^4 + 3HCl;$$

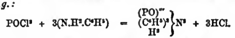
and

$$POCl^3 + 3(C^2H^5.H.O) = (C^2H^5)^3PO^4 + 3HCl.$$

With *ammonia* it forms phospho-triamide, according to the equation:

$$POCl^3 + 3NH^3 = \left.\begin{matrix}(PO)'''\\ H^6\end{matrix}\right\}N^3 + 3HCl;$$

and similarly with *aniline* and *naphthylamine*, it yields triphenyl- and trinaphthylphosphotriamide, *e.g.*:



$$POCl^3 + 3(N.H^2.C^6H^5) = \left.\begin{matrix}(PO)'''\\(C^6H^5)^3\\H^3\end{matrix}\right\}N^3 + 3HCl.$$

When added by drops to heated *zinc-ethyl*, it acts with great violence and forms a colourless viscid liquid, solidifying after a while to a vitreous mass, which when treated with water, yields insoluble oxychloride of zinc and a soluble compound of zinc-chloride with chloride of tetrethylphosphonium, $2P(C^2H^5)^4Cl.Zn''Cl^2$. (Pebal, Ann. Ch. Pharm. cxx. 194; Jahresb. 1861, p. 491.)

*Compounds of Phosphoric Oxychloride with Metallic chlorides* (Casselman, Ann. Ch. Pharm. xci. 241; xcviii. 213; Jahresb. 1854, p. 360; 1856, p. 282).—Oxychloride of phosphorus forms crystalline compounds with several metallic chlorides. The *aluminium-compound*, $AlCl^3.POCl^3$, is obtained by heating chloride of aluminium with excess of the oxychloride in a sealed tube, and separates on slow cooling in transparent colourless crystals. It melts at 165°, solidifies in the crystalline form on cooling, boils at a heat below redness, and may be passed in the state of vapour through red-hot tubes without decomposition. It deliquesces when exposed to the air, and dissolves in water, with considerable rise of temperature, and formation of alumina, hydrochloric acid, and phosphoric acid (Casselmann, Ann. Ch. Pharm. xcviii. 213; Jahresb. 1856, p. 282).—A *magnesium-compound*, $Mg''Cl^2.POCl^3$, is formed in like manner, but very slowly, and may be freed from excess of the oxychloride by prolonged heating to 150° in a current of dry air. It is inodorous; deliquescent; is decomposed by water like the preceding compound; and is resolved at a red heat into chloride of magnesium and oxychloride of phosphorus.—A *stannic compound*, $Sn^{iv}Cl^4.POCl^3$, is produced immediately, as a white crystalline mass, on bringing stannic chloride in contact with oxychloride of phosphorus. It also separates in crystals from the yellow liquid formed on treating the compound $SnCl^4.SCl^4$ with oxychloride of phosphorus. It has a peculiar odour, melts at 55°, boils at 180°, and if protected from contact with moist air, distils over unchanged. It fumes in the air and is decomposed by water, yielding stannic chloride, hydrochloric acid and phosphoric acid; if a large quantity of water is present, stannic phosphate separates out.

A compound of phosphoric oxychloride with *chloride of zinc* is produced by distilling the two substances together in an apparatus which allows the distilled liquid to flow back continually on the fused chloride of zinc; or by passing the vapour of the oxychloride over melted zinc-chloride, kept at a temperature below its boiling point. It collects in the receiver in rhombic crystals.

Oxychloride of phosphorus does not act on *chloride of copper* even when heated. *Mercuric chloride* slowly heated to 100° with the oxychloride in sealed tubes, becomes covered with colourless crystals. The chlorides of *potassium*, *sodium*, and *barium* are converted by similar treatment into gelatinous masses.

**PHOSPHORUS, SELENIDES OF.** These compounds have recently been investigated by O. Hahn (J. pr. Chem. xciii. 430; Bull. Soc. Chim. 1865, ii. 20). Berzelius showed that selenium and phosphorus unite in all proportions when heated together (*Gmelin's Handbook*, ii. 242); Bogen (Ann. Ch. Pharm. cxxiv. 57) obtained pentaselenide of phosphorus by heating 2 at. amorphous phosphorus with 5 at. selenium in a stream of carbonic anhydride; and Hahn by a similar process has obtained the compounds $P^4Se$, $P^2Se$, $P^2Se^3$, and $P^2Se^5$, analogous to the sulphides of phosphorus. A known weight of ordinary phosphorus having been dried in a bulb-tube in a stream of hydrogen, the required quantity of pulverised selenium is added and the mixture is heated: combination then takes place at temperatures above 100°, attended with evolution of light and heat.

**Hemiselenide** or **Subselenide,** $P^4Se$.—This compound, when freed from excess of amorphous phosphorus (produced by the heat) by distillation, or by straining through a cloth under water, forms a dark yellow, oily, fetid liquid which solidifies at −12°, and is converted by heat into a colourless vapour. When dry it takes fire immediately on coming in contact with the air; it is also set on fire by red fuming nitric acid. In water containing air, it becomes covered with an opaque crust, and is partly decomposed, the water taking up phosphoric acid and a selenium-compound. It dissolves easily in sulphide of carbon, but is insoluble in alcohol and ether, by which it appears to be decomposed. It is not attacked by cold alkaline solutions; but when boiled with them it is decomposed, with evolution of phosphoretted hydrogen and formation of a selenide and selenite of the alkali-metal. In solutions of metallic salts it becomes covered with a crust of metallic phosphide and selenide.

**Protoselenide of Phosphorus,** $P^2Se$, is at ordinary temperatures a light red solid body, which sublimes when heated and burns when set on fire with a bright flame and red smoke. It is permanent in dry air, but decomposes in moist air, giving off selenide of hydrogen. It is insoluble in alcohol and ether; sulphide of carbon abstracts from it variable quantities of phosphorus. Boiling potash-ley decomposes it, with evolution of selenhydric acid, and formation of a red substance containing both phosphorus and selenium.

*Metallic Seleniohypophosphites.*—By carefully heating dry mixtures of protoselenide of phosphorus and a metallic selenide in equivalent proportions, selenium-salts are obtained having the general formulæ $M^2Se.P^2Se$ or $MPSe$[*] and $M''Se.P^2Se = M''P^2Se^3$ according to the atomicity of the metal.

The *potassium-salt*, $KPSe$, is white and permanent in dry air; in moist air it exhales selenhydric acid, and becomes covered with a red crust. With de-aërated water it forms a solution which quickly decomposes, with evolution of selenhydric acid, separation of selenium, and formation of potassic phosphate. It dissolves with partial decomposition in absolute alcohol, and cannot be crystallised from this solution. The alcoholic solution added to solutions of metallic salts having an alkaline reaction, throws down easily decomposible precipitates consisting of metallic selenio-hypophosphates; the precipitates formed in like manner in acid solutions contain variable quantities of metallic selenide. Protoselenide of phosphorus fused with 2 at. selenide of potassium forms a red substance which when heated with alcoholic solution of potash, gives up selenide of potassium and leaves the white compound $KPSe$.

The seleniohypophosphites of *sodium, barium, iron, manganese, lead, copper*, and *silver* are obtained in the same manner as the potassium-salt. The preparation of those containing the heavy metals is dangerous, unless small quantities only are operated upon; larger quantities take fire even when briskly rubbed in a mortar. The seleniohypophosphites of the heavy metals, with exception of the manganous salt, are very stable, decomposing only at high temperatures. They all dissolve in nitric acid; only the manganous salt in hydrochloric acid. They are slowly decomposed by boiling alkaline solutions.

**Triselenide of Phosphorus** or **Phosphorous Selenide.** $P^2S^3$.—This compound, analogous in composition to phosphorous oxide, is a solid body of a dark ruby-red colour, and having, when pulverised, the aspect of amorphous phosphorus. When heated it is converted into a yellow vapour which condenses in films of very various colour, from light yellow to very dark red. It burns in the air with a feeble flame and red smoke; oxidises slowly in moist air; and gives off selenhydric acid when boiled with water. It is insoluble in alcohol, ether, and sulphide of carbon, but dissolves easily in caustic potash-ley, less easily in alkaline carbonates.

*Seleniophosphites*, $2M^2Se.P^2Se^3 = M^4P^2Se^5$ or $2M''Se.P^2Se^3 = M''^2P^2Se^5$[†] according to the atomicity of the metal. When 1 at. phosphorous selenide is fused with 2 at. of a metallic selenide, compounds are formed which appear to be of definite constitution, inasmuch as if a larger proportión of the phosphorous selenide be used, the excess may be extracted from the fused mass by solvents, leaving a residue having the above composition.

The *potassium-salt*, $K^4P^2Se^5$, is yellow, very hygroscopic, and decomposible by water; soluble in a mixture of alcohol and ether, less soluble in pure alcohol or pure ether, any excess of phosphorous selenide remaining undissolved. The solutions form with the salts of the heavy metals, unstable precipitates of the corresponding metallic compounds.

The yellow *sodium-salt* and the light-red *barium-salt* have been prepared by direct combination in the dry way; also the *manganese-salt*, $Mn^2P^2Se^5$, the *copper-salt*, $Cu^4P^2Se^5$, the *lead-salt*, $Pb^2P^2Se^5$, and the *silver-salt*, $Ag^4P^2Se^5$, which are dark yellow, amorphous and tolerably stable substances, dissolved or decomposed only by red fuming nitric acid, excepting the manganous salt, which is dissolved also by boiling hydrochloric acid.

**Pentaselenide of Phosphorus, Phosphoric Selenide.** $P^2Se^5$.—This compound, analogous in composition to phosphoric oxide, is more difficult of preparation than the preceding; it is necessary to use very finely divided selenium, prepared by precipitation with sulphurous acid, and to mix the substances very intimately by exposing them in a glass tube to a heat just sufficient to melt the phosphorus before subjecting them to a strong heat. It is solid, dark red, permanent in moist as well as in dry air, but decomposes when distilled. It is insoluble in sulphide of carbon; decomposed by potash-ley even in the cold.

*Seleniophosphates*, $2M^2Se.P^2Se^5 = M^4P^2Se^7$.—Pentasulphide of selenium likewise unites with metallic selenides, apparently forming salts analogous in composition to the pyrophosphates; but they are very unstable and their composition cannot be regarded as definitively established. The *potassium-salt*, $K^4P^2Se^7$, is dark-coloured, deliquescent, and immediately decomposed by water, alcohol, and ether. Hence, when added to solutions of metallic salts, it forms precipitates consisting merely of metallic phosphide and selenide. Similar remarks apply to the *sodium-salt* and to the *barium-salt*, which is of a light brick-red colour.—The *copper-salt*, $Cu^2P^2Se^7$, and the *silver-salt*, $Ag^4P^2Se^7$, are black, with metallic lustre, permanent in the air, and leave metallic phosphides when ignited; they are dissolved only by fuming nitric acid. The *lead-salt* is black; the *manganese-salt* light red.

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[*] Analogous to hypothetical anhydrous hypophosphites, $MPO$ or $M^2O.P^2O$ (p. 524).

[†] Analogous to hypothetical anhydrous phosphites, $M^4P^2O^5$ or $2M^2O.P^2O^3$.

**PHOSPHORUS, SULPHIDES OF.** When ordinary phosphorus and sulphur are heated together in the dry state or melted together under water, combination takes place between them, attended with vivid combustion and often with violent explosion. When amorphous phosphorus is used, the reaction is not explosive though still very rapid.

Six different compounds of sulphur and phosphorus have been obtained, namely $P^4S$, $P^2S$, $P^4S^3$, $P^2S^3$, $P^2S^5$ and $P^2S^{12}$, the first, second, fourth and fifth being analogous to the selenide above described. They may all be formed by heating the two bodies together in the required proportions; but the trisulphide and pentasulphide are more easily prepared by warming the protosulphide with additional proportions of sulphur. Moreover, the two lower sulphides, $P^4S$ and $P^2S$, exhibit isomeric modifications, each being capable of existing as a colourless liquid and as a red solid. The proto-, tri- and pentasulphides of phosphorus unite with metallic sulphides, forming sulphur-salts analogous to the selenium-salts above described. Our knowledge of the sulphides of phosphorus is due chiefly to the researches of Berzelius. (*Traité de Chimie*, Paris, 1845, i. 815; *Gmelin's Handbook*, ii. 209.)

**Hemisulphide** or **Subsulphide,** $P^4S$. *Hyposulfide phosphoreux. Phosphorsulfuret.* α. Colourless liquid modification.—This modification is prepared by melting 4 at. phosphorus and 1 at. sulphur under hot water, or by heating them in the dry state in a sealed tube to about 60°, after the oxygen of the enclosed air has been taken up by the phosphorus; also by digesting phosphorus in an alcoholic solution of potassium-persulphide (liver of sulphur).

The product thus obtained is, at ordinary temperatures, a transparent, colourless liquid, having the consistence of a fixed oil. At a few degrees below 0° it solidifies, forming a mass of slender, colourless crystals. It fumes in the air, and exhales the odour of phosphorus. In an atmosphere free from oxygen, it may be distilled without alteration. It readily takes fire in the air, particularly when absorbed by porous bodies. It is insoluble in alcohol and ether; but these liquids are gradually altered by it, even out of contact of air, and the new products dissolve in the liquid, while the remaining sulphide undergoes no alteration, but merely diminishes in volume. Oils, both fixed and volatile, dissolve it in small quantity: the solution shines in the dark, and gives off slight fumes when in contact with the air. Subsulphide of phosphorus dissolves, with the aid of heat, an additional quantity of phosphorus, but deposits it again in the form of rhombic dodecahedrons on cooling.

It may be preserved without alteration in a bottle filled with boiled water and well corked; but in water impregnated with air, the phosphorus gradually oxidises and is converted into phosphoric acid; hence the liquid acquires an acid reaction. When boiled with *water*, it slowly exhales sulphydric acid.—When digested in solution of *potash* or *soda*, it yields a phosphate, sulphydrate, and polysulphide of the alkali-metal; and there finally remains a quantity of phosphorus free from sulphur, which solidifies on cooling.

β. Red Modification. Formed when the preceding substance, or the liquid protosulphide of phosphorus, is gently heated in contact with an electro-positive metallic sulphide. It is best prepared as follows:—A layer of anhydrous carbonate of sodium two inches thick is placed in a tube six or eight inches long, and a quantity of liquid protosulphide of phosphorus poured upon it, drop by drop, till the carbonate of sodium is slightly impregnated with the liquid throughout. The tube is then closed with a cork, through which a gas-delivery tube passes, and immersed in a sand-bath, to such a depth that the level of the sand may be a little above that of the salt within the tube. The sand-bath is raised to a temperature sufficient to maintain the water in a vessel placed beside the tube in a state of constant ebullition. On withdrawing the tube from the sand from time to time, it is found that the mass first turns yellow without fusing, and afterwards assumes a red colour, which commences at the bottom, and gradually extends itself upwards, increasing at the same time in intensity. Above the saline mass there is deposited, on the sides of the tube, a spontaneously inflammable sublimate of phosphorous anhydride, formed at the expense of the air already contained in the tube, and of that which enters slowly and insensibly through the gas-delivery tube. As soon as the red colour ceases to spread any further, the tube is withdrawn from the sand-bath and left to cool. When perfectly cold, it must be scratched with a file, a line or two below the upper limit of the red tint, then broken at that point, and the two ends immediately thrown into water, as the surfaces of the saline mass would take fire instantly on coming in contact with the air. The water dissolves out a quantity of sulphophosphite, phosphate and carbonate of sodium, while a red powder is left behind. This is to be well washed with cold water previously freed from air by boiling, and then left to dry on the filter placed upon filtering paper to absorb the moisture. The powder thus obtained is the red hemisulphide of phosphorus. To insure success in the preparation, it is necessary to use the exact proportions of alkali and sulphide of phosphorus required, and to avoid the application of too great a heat. If the quantity of protosulphide is too small, phosphorus is set free; and when it is too great, other red compounds are produced containing less phosphorus. If the temperature rises too high, the mass blackens without fusing; the phosphorus reduces the carbonic acid, and a quantity of charcoal is obtained, impregnated with phosphorus and mixed with phosphate, metaphosphate, and persulphide of sodium.

Red subsulphide of phosphorus is a crystalline opaque powder of a beautiful deep vermillion-colour. It has neither taste nor smell. Heated in a small distillatory apparatus filled with hydrogen gas, it volatilises without fusing, and condenses in the receiver as colourless liquid subsulphide, but this change does not take place till the temperature is raised above the boiling point of the latter. Pure nitric acid of density 1·22 has no action on this compound at first; but, after a certain time, the subsulphide dissolves suddenly and with great violence. By less concentrated nitric acid, it is not attacked without the aid of heat.

**Protosulphide,** $P^2S$.—*Sulphohypophosphoric acid. Hyposulfide phosphorique. Unterphosphoriges Sulfid. Phosphorsulfür.* α. Colourless liquid modification.—Prepared by fusing together one atom of sulphur and two atoms of phosphorus, in the same manner as in the preparation of the subsulphide.

It is a transparent, yellow, strongly refractive liquid, not very mobile; has a strong and repulsive odour, recalling that of phosphorous acid and of chloride of sulphur. It may be distilled without alteration in an atmosphere free from oxygen. It is colourless in the gaseous state. At a certain number of degrees below 0° it solidifies and forms a colourless mass of small interlaced crystals; but its crystallising point is lower than that of the subsulphide. It fumes in the air and is luminous in the dark; likewise emits light when vaporised in nitrogen or hydrogen gas free from oxygen. It adheres strongly to dry solid bodies: if a small quantity of it gets attached to the fingers, it cannot be removed by water, even with the aid of soap, unless the skin be previously rubbed with oil. It takes fire easily in the air at a slightly elevated temperature, burning with a bright flame, like that of phosphorus, and emitting a thick smoke. It does not take fire spontaneously when a drop of it is let fall on a solid body; but when absorbed by a porous body and exposed to the air, it soon becomes heated and takes fire.

*Decompositions.*—1. When protosulphide of phosphorus evaporates slowly in a confined space (as a bell-jar) filled with moist air, which is slowly but continually renewed, it is converted by oxidation into sulphuric and phosphoric acids, which are deposited in the form of aqueous solution on the sides of the vessel and around the liquid itself.—2. In a limited atmosphere of dry air slowly and continually renewed (as in a glass tube imperfectly closed by a cork) it is gradually converted, in the course of three weeks, into phosphorous anhydride, which forms a white mass in the upper part of the tube, and takes fire on removing the cork,—persulphide of phosphorus (p. 605), which crystallises at the bottom of the liquid,—and a brown substance, which collects on the sides of the tube, in a layer of continually increasing thickness, and is resolved by digestion in water, into phosphoric and sulphuric acids, and hydrated suboxide of phosphorus.—3. Placed in a tube imperfectly closed by a cork, and heated in a sand-bath, it is converted into a white, spontaneously inflammable mass, consisting, for the most part, of phosphorous anhydride.—4. *Water* has but very little action on this liquid. Under de-aërated water it may be kept almost unchanged; in water containing air it emits after a while the odour of sulphydric acid, and deposits finely divided sulphur.—5. With *alcohol, ether,* and *oils,* both fixed and volatile, it behaves like the subsulphide.—6. It is decomposed by digestion with caustic *alkalis,* the products being a phosphate, sulphydrate, and polysulphide of the alkali-metal.—7. When it is heated gently in contact with a *metallic sulphide* in an atmosphere free from oxygen, great heat is evolved, and a considerable portion of the liquid distils over with almost explosive violence: at the same time a sulphohypophosphite of the metal is produced in which the sulphide of phosphorus exists in the red modification.—8. On digesting this compound with metallic solutions, sulphides of the metal containing variable quantities of sulphohypo-sulphite are slowly deposited, the variation in the results arising from oxidation of the phosphorus at the expense of the metallic solution, the quantity thus oxidised depending upon the temperature and the concentration of the solution. From solutions of easily reducible metals, such as *silver*, nothing but a sulphide of the metal is precipitated. *Copper* gives a precipitate of sulphohypophosphite. With ammoniacal solution of *cuprous chloride*, a dark-red precipitate is obtained, resembling cuprous oxide.

β. Red Modification. Obtained by decomposing sulphohypophosphite of manganese with hydrochloric acid:

$$Mn''S.P^2S \;+\; 2HCl \;=\; Mn''Cl^2 \;+\; H^2S \;+\; P^2S.$$

It is an orange-coloured powder, inclining to yellow, tasteless and inodorous; unalterable both in air and water. By dry distillation it is converted into the liquid protosulphide, without previous fusion. It assumes a darker colour when heated, but regains its original tint on cooling. Takes fire in the air at a temperature near 100°, and burns with a very bright flame, emitting a thick smoke.

When it is digested in excess of strong caustic *potash* at ordinary temperatures, phosphoretted hydrogen gas of the less inflammable variety is disengaged, and the alkali dissolves small quantities of phosphoric acid and trisulphide of phosphorus. On the application of heat, the whole is dissolved, yielding the same products as the liquid modification (p. 600). Caustic ammonia dissolves it, but not without great difficulty, forming a yellow solution.

***Sulphohypophosphites***, $M^2S.P^2S$ or $MPS$.—Protosulphide of phosphorus unites with metallic sulphides, forming compounds analogous to the seleniohypophosphites (p. 598). They may be formed, as above mentioned, either by precipitation or in the dry way; but the latter method affords much purer products than the former.

*Cupric salt*, $Cu''P^2S^2 = Cu''S.P^2S$.—To prepare this compound, precipitated sulphide of copper, dried by gentle heating in a stream of sulphydric acid gas, is moistened with liquid protosulphide of phosphorus in a tube having two bulbs blown on it. On applying a gentle heat, combination takes place attended with great rise of temperature, and the greater part of the excess of protosulphide distils off: the rest may be expelled by a gentle heat. The remaining cupric sulphohypophosphite is a black-brown mass yielding a lighter powder by trituration, and usually containing a little admixed sulphide of copper. It dissolves slightly in boiling hydrochloric acid, and is oxidised and dissolved by nitro-muriatic acid. By distillation, it gives off a small quantity of liquid protosulphide of phosphorus, then, at an incipient red heat, a sulphide of phosphorus containing a large proportion of sulphur, leaving liver-coloured cuprous sulphohypophosphite, $Cu^2S.P^2S$ or $CuPS$. This latter compound cannot be obtained by direct combination in the dry way. It is produced, however, by the action of the liquid protosulphide on an ammoniacal solution of cuprous chloride. It is not altered by gentle ignition in a close vessel; but when heated in contact with the air, it burns without flame, giving off sulphurous anhydride.

*Ferrous salt*, $Fe''S.P^2S = Fe''P^2S^2$.—Prepared in the same manner as the cupric salt, using artificially prepared sulphide of iron in the state of fine powder. It is a coal-black powder generally containing a little sulphophosphite of iron.

*Manganous salt*, $Mn''P^2S^2 = Mn''S.P^2S$.—Prepared like the copper-salt. It is green, lighter than manganous sulphide, is completely decomposed by dry distillation, and burns in the air with a strong phosphorus-flame. It is decomposed by boiling hydrochloric acid, manganous sulphide dissolving, and protosulphide of phosphorus remaining in the red modification.

*Mercuric salt*, $Hg''S.P^2S$.—Finely divided cinnabar unites at a gentle heat with protosulphide of phosphorus, and after the excess of the latter has been removed by distillation in a stream of hydrogen, there remains a dingy red mass, yielding a yellow powder. It is easily decomposed by a stronger heat, with liberation of metallic mercury and formation of a yellowish-white powder (p. 603). A basic salt, $2Hg''S.P^2S$, is obtained by heating mercuric sulphophosphite (p. 603) in a retort.

*Silver-salt*, $AgPS$ or $Ag^2S.P^2S$.—Formed when spongy silver (obtained by reducing the chloride with silver in the wet way, exhausting the mass with cold hydrochloric acid, and washing with water) is treated with protosulphide of phosphorus at a gentle heat. Combination then takes place with some violence, and sulphohypophosphite of silver is formed, together with a higher sulphide of phosphorus, which must be removed by distillation in a stream of hydrogen. The silver-sulphohypophosphite may also be obtained, mixed with a large quantity of silver-sulphide, by warming the latter, recently precipitated, with liquid protosulphide of phosphorus, and treating the mixture with warm nitric acid, which dissolves only the uncombined sulphide of silver. The compound is black, but yields by trituration a dark brown powder with a tinge of violet.

By dry distillation it becomes semifluid and swells up strongly, the sulphide of phosphorus passing over and the sulphide of silver remaining. The compound is scarcely attacked by hot nitric acid.

*Tritosulphide of Phosphorus*, $P^4S$.—This substance, which may be regarded as a compound of the hemi- and proto-sulphides, ($P^4S + P^2S = 2P^3S$) is prepared as follows. Precipitated sulphide of zinc is treated with liquid protosulphide of phosphorus, as in the preparation of sulphohypophosphite of copper, whereby it is converted, first into yellow sulphohypophosphite of zinc, and afterwards into a red compound consisting of $(Zn''S.P^4S).(Zn''S.P^2S)$; and on treating this compound with strong hydrochloric acid, sulphide of zinc dissolves, and the tritosulphide of phosphorus remains in the form of a bright red powder, tasteless, inodorous, and permanent in the air. It takes fire at about 50°, burning with a phosphorus-flame. When submitted to dry distillation, it first turns black, then distils without previous fusion; the distillate contains the two liquid sulphides $P^4S$ and $P^2S$, perhaps combined with one another. Cold potash-ley decomposes the compound, with evolution of the less inflammable variety of phosphoretted hydrogen.

**Sesquisulphide of Phosphorus,** $P^4S^3$.—This compound is produced by heating 1 at. sulphur with 2 or more atoms of amorphous phosphorus, and may be freed from excess of the latter by solution in sulphide of carbon, whence it crystallises in yellow right rhombic prisms of 81° 30′. It melts at 142° to a reddish mass, and sublimes at 260° in forms belonging to the regular system: hence it is dimorphous. It is more soluble in sulphide of carbon than sulphur; slightly soluble in trichloride and sulphochloride of phosphorus; dissolves also, but with decomposition, in alcohol and ether. It is permanent in the air at ordinary temperatures, and in cold water, and is but slowly decomposed by hot water. Heated in the air to about 100° it takes fire. It dissolves in cold dilute nitric acid, leaving a little sulphur; completely in nitromuriatic acid and in chlorine-water. It dissolves in sulphide of potassium or sodium, probably forming definite compounds. It is decomposed by aqueous potash, giving off hydrogen and phosphoretted hydrogen, and forming sulphide and phosphite of potassium. Heated to 200° with hydrate of lead it forms sulphide of lead. (G. Lemoine, Bull. Soc. Chim. 1864, [1] 407.)

**Trisulphide of Phosphorus,** $P^2S^3$.—*Sulphophosphorous acid. Phosphorous sulphide. Sulfide phosphoreux. Phosphorsulfid.*—Discovered by Serullas, who obtained it by the action of sulphydric acid on trichloride of phosphorus, but did not further examine it. Berzelius prepared it by the following methods: 1. Red protosulphide of phosphorus is mixed with the quantity of sulphur required to convert it into the trisulphide (1 at. $P^2S$ to 2 at. S), and the mixture is heated in a small retort. The heat evolved at the moment of combination is so great, that a small portion of the mass is volatilised with violence. The whole then fuses uniformly, and ultimately sublimes in the form of a transparent crystalline substance of a pale lemon-yellow colour. If the distillation be interrupted before the whole is volatilised, the unsublimed portion retains a reddish colour while hot, but on cooling acquires the same colour as the sublimed portion.—2. One atom of sulphohypophosphite of manganese is intimately mixed with 2 atoms of sulphur, and the mixture heated in a small retort in an atmosphere free from oxygen, till nothing but protosulphide of manganese remains: trisulphide of phosphorus is then obtained in the form of a sublimate:

$$Mn''S.P^2S + S^2 = Mn''S + P^2S^3.$$

If a sulphohypophosphite be employed, the base of which does not so readily give up its sulphur-acid—the silver-salt for example—only half of the trisulphide of phosphorus sublimes, while the rest remains in combination, in the form of sulphophosphite of silver.

Kekulé (Ann. Ch. Pharm. xc. 310) prepares this compound by carefully fusing amorphous phosphorus with the requisite quantity of sulphur in an atmosphere of carbonic anhydride; combination then takes place without explosion, but nevertheless with great rise of temperature, so that part of the product is sublimed.

Trisulphide of phosphorus is a solid substance, of a pale yellow colour. After fusion or sublimation, it remains soft, like plastic sulphur, and does not become opaque till it hardens. It melts at 200° (Lemoine) and sublimes at a temperature below the subliming point of sulphur. When heated in the air, it burns with a whitish-yellow flame, and diffuses a thick smoke. In moist air, it decomposes rapidly, becoming white and assuming an acid reaction, in consequence of the formation of phosphoric acid: at the same time it acquires a bitter and hepatic taste. This decomposition in the air takes place so rapidly that the substance can only be preserved in vessels hermetically sealed. The unsublimed reddish trisulphide decomposes in the same way.

Trisulphide of phosphorus is rapidly dissolved by the fixed caustic alkalis and by ammonia. The solutions have a pale yellow colour, and when treated with acids yield a light, flocculent, and nearly white precipitate, which falls down slowly, and has a pale yellow colour when collected in a mass: this precipitate may be washed and dried. Trisulphide of phosphorus in this state is less rapidly decomposed by exposure to the air than that which has been fused or sublimed. It is uncertain whether the difference thus produced by the influence of an alkali depends upon an isomeric modification. Trisulphide of phosphorus is easily dissolved in the cold by carbonate of potassium or sodium, but deposits sulphur at the same time—a proof that decomposition takes place.

*Sulphophosphites.*—1 atom of trisulphide of phosphorus unites with 2 atoms of a metallic protosulphide, forming salts having the composition $2M^2S.P^2S^3 = M^4P^2S^5$ and $2M''S.P^2S^3 = \overset{''}{M}{}^2P^2S^5$, according to the atomicity of the metal. These compounds are produced, together with free trisulphide of phosphorus, by triturating the corresponding sulphohypophosphites with the requisite quantity of sulphur:

$$2(M^2S.P^2S) + S^4 = 2M^2S.P^2S^3 + P^2S^3.$$

They are also formed by heating protosulphide of phosphorus with metallic polysulphides, just as certain lower oxides of metalloïds are converted by heating with metallic peroxides into higher oxides of an acid character, which then unite with the bases formed by reduction of the peroxides. Many sulphophosphites are decomposed by heat, giving off trisulphide of phosphorus, and leaving the metallic sulphide.

*Cupric Sulphophosphite*, $\overset{''}{Cu}{}^2P^2S^5 = 2Cu''S.P^2S^3$.—Produced by precipitating an ammoniacal solution of cupric sulphate with soda-liver of sulphur, and treating the washed precipitate ($CuS^2$), after drying in vacuo, with liquid protosulphide of phosphorus. Combination then takes place, attended with evolution of heat, and the excess of protosulphide may be expelled in a stream of hydrogen. The cupric sulphophosphite then remains as a dark yellow powder which burns with a phosphorus-flame when heated in the air. When subjected to dry distillation, it gives off sulphur and leaves a dark brown basic cuprous sulphohypophosphite, $2Cu^2S.P^2S$.

*Ferrous Sulphophosphite*, $\overset{''}{Fe}{}^2P^2S^5 = 2Fe''S.P^2S^3$.—Obtained by moistening finely divided iron pyrites ($FeS^2$) in a bulb-apparatus with liquid protosulphide of phosphorus, and applying a gentle heat. After the excess of the protosulphide has distilled off, the sulphophosphite remains as a dark yellow mass, having a faint metallic lustre. It dissolves in boiling hydrochloric acid, and decomposes in contact with moist air, emitting the odour of sulphydric acid. By dry distillation it gives off sulphur, and leaves the black-brown compound, $2Fe''S.P^2S$.

*Mercuric Sulphophosphite*, $Hg^2P^2S^5 = 2Hg''S.P^2S^3$.—Produced by heating the corresponding sulphohypophosphite in a retort having its neck closed by a cork, to about the boiling point of sulphur. A black mass then sublimes, containing numerous globules of mercury, and mercuric sulphophosphite remains, as a yellowish-white mass, which at a higher temperature is resolved into basic mercuric sulphohypophosphite and mercuric sulphophosphate:

$$2(2Hg''S.P^2S^3) = 2Hg''S.P^2S + 2Hg''S.P^2S^5.$$

*Sulphophosphite of Silver*, $Ag^4P^2S^5 = 2Ag^2S.P^2S^3$.—Produced by heating finely divided silver with phosphorus and sulphur in an atmosphere of hydrogen, the combination taking place with great violence. The product after being heated forms a grey lump, yielding a light yellow powder. Nitric acid decomposes it easily, and dissolves it without separation of sulphur.

**Pentasulphide of Phosphorus,** $P^2S^5$.—*Sulphophosphoric acid. Phosphoric Sulphide. Sulfide phosphorique. Phosphorspersulfid.*—This compound, analogous to phosphoric oxide or anhydride, is produced: 1. By direct combination, when sulphur and phosphorus are heated together above 100° in an atmosphere free from oxygen. With ordinary phosphorus the combination is attended with a very violent and dangerous explosion, but when amorphous phosphorus is used, no explosion takes place, though great heat is evolved.—2. By heating 1 at. solid protosulphide of phosphorus with 4 at. sulphur, in an atmosphere free from oxygen. The act of combination is attended with a sudden disengagement of heat, by which a portion of the substance is rapidly sublimed; but there is no explosion or production of light.—3. When 1 at. sulphohypophosphite of manganese is heated with 4 at. sulphur, the pentasulphide sublimes at a gentle heat, leaving protosulphide of manganese. Sulphohypophosphite of silver heated with 4 at. sulphur yields sulphophosphate of silver, while half of the pentasulphide of phosphorus sublimes.—4. Pentasulphide of phosphorus is likewise formed when the liquid protosulphide is heated in a current of sulphydric acid gas. A pale liquid distils over, which is a solution of the pentasulphide in the liquid protosulphide, and yields a small quantity of the former in crystalline scales.

Pentasulphide of phosphorus is of a pale yellow colour, like the trisulphide, but crystallises. When it is sublimed very slowly and in such a manner that it can form isolated crystals, these crystals are transparent, and appear perfectly colourless when thin: their faces are deeply striated. When the liquid pentasulphide is distilled, it assumes a crystalline form in solidifying, and is then easily detached from the glass. When solidified by sudden cooling, it does not crystallise, but forms a mass, sometimes yellow and transparent, sometimes whitish and opaque. When obtained by fusion from the red protosulphide of phosphorus, it does not crystallise on cooling, unless it be first sublimed. After being fused and heated to the boiling point, it has a deeper colour, like that of sulphur. Its boiling point is higher than that of sulphur, and the colour of its vapour is a less intense yellow than that of sulphur vapour. When heated in the air, it burns with a pale phosphoric flame, and diffuses a large quantity of smoke. In moist air, it is decomposed almost as easily as the trisulphide, and transformed into a white mass impregnated with phosphoric acid.

*Sulphophosphates.* Pentasulphide of phosphorus dissolves in caustic alkalis and in ammonia, forming pale-yellow solutions, from which acids precipitate sulphur with abundant evolution of sulphydric acid. It appears as if no alkaline sulphophosphate could exist in contact with water. The carbonates of potassium and sodium slowly dissolve the pentasulphide in the cold, producing at the same time an abundant deposit of flakes of sulphur. On heating the liquid to about 60°, the sulphide of phosphorus dissolves with violence, and inodorous carbonic anhydride is evolved: no deposition of sulphur takes place. When boiled, the liquid evolves carbonic anhydride and sulphydric acid gases together.

*Sulphophosphate of potassium* is obtained in the dry way, mixed with trisulphide of phosphorus, by passing phosphoretted hydrogen over the heated compound $K^4S^7$ (H. Rose). The colourless salt thus produced is soluble in water, but is decomposed thereby, yielding sulphydric acid and phosphate of potassium.

The neutral sulphophosphates of the heavy metals have the composition $\overset{\prime\prime}{M}{}^4P^2S^7 = 2M''S.P^2S^5$ analogous to that of the pyrophosphates. They are produced by heating basic sulphohypophosphites with the corresponding quantity of sulphur: $2M''S.P^2S + S^4 = 2M''S.P^2S^5$. When heated they behave like the sulphophosphites, many of them giving off undecomposed pentasulphide of phosphorus, and leaving a pure metallic sulphide: *e. g.* the zinc, manganous and ferrous salts; others are decomposed by heat into sulphur and a residue of sulphohypophosphite The sulphophosphates are permanent in dry air, but in moist air they exhale the odour of sulphydric acid. When heated in the air, they burn with a phosphorus-flame; but few of them have been specially examined.

The *cupric salt* $\overset{\prime\prime}{Cu}{}^2P^2S^7$, obtained by gently heating the compound $2Cu''S.P^2S$ with 4 at. sulphur, has a pale yellow colour; but if too strong a heat has been applied in its preparation, part of the phosphoric sulphide goes off and a basic sulphophosphate $\overset{\prime\prime}{Cu}{}^2P^2S^7.6Cu''S$ remains behind.

The *mercuric salt* is obtained by the dry distillation of mercuric sulphohypophosphite or sulphophosphite. The former, if somewhat strongly heated in a retort, first gives off metallic mercury, and then yields mercuric sulphophosphite, which sublimes in transparent, highly lustrous, pale yellow needles. If on the other hand the sulphohypophosphite be very gently heated for a considerable time, so that mercuric sulphophosphite may be first formed, and this salt be then heated to sublimation, a sublimate of pure mercuric sulphophosphate is obtained in red shining crystals very much like cinnabar, but of somewhat lighter colour and yielding a brown-yellow powder.

Alcoholic Sulphophosphates.—A triethylic sulphophosphate, $(C^2H^5)^3PS^4 = 3C^4H^{10}S.P^2S^5$, analogous in composition, not to the pyrophosphates, but to the normal orthophosphates, has been already described (p. 593).

**Sulphoxyphosphates,** $M^3PSO^3$ or $3M^2O.P^2S^2O^3$ and $\overset{\prime\prime}{M}{}^3P^2S^2O^6 = 3M''O.P^2S^2O^3$ (Wurtz, Ann. Ch. Phys. [3] xx. 472).—Sulphoxyphosphate of sodium is obtained by the action of caustic soda-solution on phosphoric sulphochloride:

$$PSCl^3 + 6NaHO = Na^3PSO^3 + 3NaCl + 3H^2O.$$

When the materials are put into a retort, and subjected to the heat of a water-bath, ebullition takes place, and part of the sulphochloride distils over into the receiver; and when the whole of the sulphochloride has disappeared, and the liquid is allowed to cool, it generally forms into a solid crystalline mass: this is to be drained, and the crystals purified by repeated solution in water and crystallisation. The soda must be in excess, because the free acid in solution is readily decomposed into phosphoric and sulphydric acids:

$$H^3PSO^3 + H^2O = H^2S + H^3PO^4.$$

Sulphoxyphosphate of sodium is readily soluble in boiling water, and crystallises on cooling in brilliant six-sided tables. The solution has a strong alkaline reaction. Chlorine, bromine, and iodine decompose it immediately, with separation of sulphur and formation of disodic orthophosphate. The weakest acids added to the solution liberate sulphoxyphosphoric acid, which is immediately decomposed on boiling.

The sulphoxyphosphates of *barium*, *strontium*, and *calcium* are insoluble; the *nickel-* and *cobalt-salts* turn black on boiling; the *lead-salt* is white when newly formed, but turns black in a few hours from separation of lead-sulphide.

*Ethyl-sulphoxyphosphoric* or *Ethyl-sulphophosphoric acid*, $(C^2H^5)H^2PSO^3$, produced by the action of alcoholic potash or soda on phosphoric sulphochloride (Cloez), and *diethyl-sulphophosphoric acid*, $(C^2H^5)^2HPSO^3$, by the action of pentasulphide of phosphorus on alcohol (Carius), have been already described under *phosphoric ethers;* also certain ethyl-phosphoric ethers in which 2 at. oxygen are replaced by sulphur (pp. 591-593).

**Persulphide of Phosphorus.** This compound, which may be obtained by direct combination of its elements, was first recognised by Dupré, who assigned to it the formula $P^2S^6$. Berzelius afterwards gave the formula $P^2S^{12}$. The cause of this great difference has not been ascertained.

When 1 pt. phosphorus is fused with 1 pt. or more of sulphur, the mass separates on cooling into liquid protosulphide and crystals of the persulphide. The best mode of obtaining the persulphide regularly crystallised is to dissolve 1 atom of sulphur in 1 atom of liquid protosulphide of phosphorus by the heat of a water-bath, and then leave the vessel, carefully closed, to cool in the bath. The crystals thus obtained are few in number, but of considerable size, yellow and shining, and frequently present numerous facets, like those of native sulphur. Some are cleavable in the direction of the laminæ. They are impregnated with protosulphide of phosphorus, which adheres to them obstinately, and causes them to emit slight fumes from the surface of a recent fracture. To free the crystals from the protosulphide, they must be dried, reduced to small pieces, and placed between folds of bibulous paper under a bell-jar, and by the side of a small dish containing water, the edge of the bell-jar being slightly raised by the insertion of a small piece of wood to allow of the renewal of the air within it. In this manner, the protosulphide adhering to the crystals is converted into phosphoric acid, sulphuric acid, and persulphide of phosphorus. Some time elapses before the change is complete; but sooner or later the odour of the protosulphide disappears entirely. The crystals are then to be washed and dried over oil of vitriol.

The crystals thus obtained may be exposed to the air for a long time, without diminution of the lustre of the crystalline facets; but after a while, they redden litmus paper when placed upon it. In a stoppered bottle filled with dry air they may be preserved for any length of time without alteration. They fuse at a temperature near the melting point of sulphur, and then distil over without separation of protosulphide of phosphorus. The distilled product does not crystallise, but remains soft long after cooling. If the persulphide, when subjected to distillation, is not quite free from protosulphide, an explosion takes place on the application of heat, arising from the formation of pentasulphide.

The persulphide dissolves in caustic alkalis, behaving like a mixture of sulphur and protosulphide of phosphorus, and forming phosphate, hyposulphite, and persulphide of the alkali metal. By fusion at a gentle heat, it may be made to take up an additional quantity of sulphur. (Berzelius.)

**PHOSPHORUS, SULPHOBROMIDE OF.** $PSBr^3$. (Bandrimont, Bull. Soc. Chim. 1861, p. 118.)—Produced: 1. By the action of dry sulphydric acid gas on the pentabromide:

$$PBr^5 + H^2S = PSBr^3 + 2HBr.$$

2. By distilling a mixture of pentabromide of phosphorus and sulphide of antimony:

$$3PBr^5 + Sb^2S^3 = 3PSBr^3 + 2SbBr^3.$$

3. By direct combination of 1 at. tribromide of phosphorus with 1 at. sulphur.

It is a solid, yellowish, very dense mass, which fumes in the air, has a nauseating odour, is partially decomposed by heat, and slowly but completely by water.

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**PHOSPHORUS, SULPHOCHLORIDE OF.** $PSCl^3$.—This compound, the analogue of phosphoric oxychloride, was discovered by Serullas (Ann. Ch. Phys. [2] xlii. 25), who obtained it by the action of sulphydric acid gas on the pentachloride:

$$PCl^5 + H^2S = 2HCl + PSCl^3.$$

The product is purified by distillation.

It is likewise formed, together with other products, by the action of pentachloride of phosphorus on various metallic sulphides (Weber, p. 514), and by that of sulphur on the pentachloride (Wöhler and Hiller). Gladstone (Chem. Soc. Qu. J. iii. 5), by melting 3 pts. pentachloride of phosphorus with 1 pt. sulphur, obtained a colourless liquid boiling at 100°, and apparently consisting of $PCl^5S^2$, or, according to Schiff (Ann. Ch. Pharm. ci. 309), of $PSCl^3.SCl^2$.

According to Bandrimont (Bull. Soc. Chim. 1861, p. 117), the sulphochloride is most easily prepared by the action of pentachloride of phosphorus on trisulphide of antimony:

$$3PCl^5 + Sb^2S^3 = 2SbCl^3 + 3PSCl^3.$$

About 30 grms. of phosphorus is converted into pentachloride in a large flask; the flask is then taken out into the open air, its neck surrounded with a wet cloth, and 115 grms. of antimonious sulphide gradually added, with frequent agitation, till all the pentachloride has disappeared and a slight excess of antimonious sulphide is present. The resulting liquid, which is hot from the violence of the reaction, is then decanted into a dry retort and distilled at 125° to 135°. To purify the distillate from chloride of antimony, pentachloride of phosphorus, and chloride of arsenic (resulting from arsenic in the sulphide of antimony), it is cooled to a low temperature and agitated with a dilute solution of sodium-sulphide. The chlorosulphide of phosphorus is then separated from the alkaline liquid by a tap-funnel, carefully dried by chloride of calcium, filtered through asbestos, and finally distilled from a dry retort. The product amounts to 120 grms.

Sulphochloride of phosphorus is a colourless, rather mobile, oily liquid, having an intensely pungent odour, aromatic when diluted; the vapour irritates the eyes strongly. Sp. gr. = 1·631 at. 22°. Boiling-point 124·25° (Bandrimont); 126—127° (Cahonrs). Vapour-density = 5·963 at 168°; 5·879 at 244°; 5·878 at 298° (Cahours); calc. (2 vol.) = 5·932. The vapour burns with difficulty.

The sulphochloride is slowly decomposed by *water*, yielding phosphoric, hydrochloric, and sulphydric acids, and fumes slightly in moist air. It is decomposed by hot *nitric acid*. When heated with aqueous *caustic alkalis*, it is converted into a salt of sulphoxyphosphoric acid $H^3PSO^3$ (Wnrtz, p. 604). With *alcohol* it yields ethyl-sulphoxyphosphoric acid $(C^2H^5)H^2PSO^3$ (p. 591). With aqueous *ammonia*, it forms sulphoxyphosphamic or thiophosphamic acid, an acid which may be derived from sulphoxyphosphoric or thiophosphoric acid by the substitution of $NH^2$ for HO; or if the ammonia is very strong, or if ammonia-gas acts on the sulphochloride first and water afterwards, the product is sulphoxyphosphodiamic or thiophosphodiamic acid, derived in like manner from thiophosphoric acid by the substitution of 2 at. $NH^2$ for 2 at. HO; thus:

$$PSCl^3 + 3H^2O = 3HCl + \underset{\text{Thiophosphoric acid.}}{PH^3SO^3.}$$

$$PSCl^3 + NH^3 + 2H^2O = 3HCl + \underset{\text{Thiophosphamic acid.}}{P(NH^2)H^2SO^2.}$$

$$PSCl^3 + 2NH^3 + H^2O = 3HCl + \underset{\text{Thiophosphodiamic acid.}}{P(NH^2)^2HSO.}$$

*Dry ammonia-gas* appears to act on sulphochloride of phosphorus by removing 2 atoms of chlorine and leaving 2 atoms of amidogen in their place; thus:

$$PSCl^3 + 4NH^3 = 2NH^4Cl + P(NH^2)^2ClS.$$

The latter compound has not yet been separated from the accompanying chloride of ammonium; but, supposing it to be formed, the production of thiophosphodiamic acid from it by means of water may be supposed to take place as shown by the equation:

$$PS(NH^2)^2Cl + H^2O = HCl + P(NH^2)^2HSO$$

(Gladstone and Holmes, Chem. Soc. J. xviii. 7); see Thiophosphamic acids.—Schiff (Jahresb. 1857 p. 99) supposes that sulphochloride of phosphorus is converted by dry ammonia-gas into sal-ammoniac and sulphophosphotriamide, according to the equation:

$$PSCl^3 + 4NH^3 = NH^4Cl + 2HCl + \left.\begin{matrix}PS)'''\\H^6\end{matrix}\right\} N^3:$$

and by aniline in like manner into hydrochlorate of aniline and sulphophosphotriphenyltriamide; but these results have not been established by analysis.

With *acetate of potassium* the chlorosulphide appears to yield sulphide of acetyl. (Baudrimont.)

**PHOSPHORUS, TELLURIDE OF.** When pulverised tellurium is heated with phosphorus, part of the latter burns away, while another portion melts with the tellurium to a black amorphous mass, which gives off fumes of phosphorous anhydride in the air even when the tellurium is in large excess. (Oppenheim, Jahresb. 1857, p. 214.)

**PHOSPHORUS-BASES, ORGANIC.** Paul Thénard in 1846 and 1847, by acting on heated phosphide of calcium with gaseous chloride of methyl, obtained several compounds, which may be viewed as phosphides of hydrogen having the hydrogen more or less replaced by methyl, viz. 1. A spontaneously inflammable fetid liquid, $(CH^3)^2P$, analogous in composition to the liquid phosphide of hydrogen, $H^2P$, and to cacodyl, $(CH^3)^2As$.—2. A spontaneously inflammable gas, $CH^5P = (CH^3)H^2P$, analogous to methylamine, and forming a solid compound with hydrochloric acid.—3. A mobile strongly basic liquid, $C^3H^9P = (CH^3)^3P$, analogous to trimethylamine, and boiling at 40°.—4. A yellow non-volatile solid, $CH^3P^2$, analogous to the solid phosphide of hydrogen, $HP^2$, produced, together with the liquid compound (3), by the continued action of hydrochloric acid gas on the first-mentioned compound, $(CH^3)^2P$.—These compounds were, however, but imperfectly studied by their discoverer: for the mode of preparation above mentioned was dangerous, and did not yield them in quantity sufficient for satisfactory investigation. Moreover, at the time of their discovery there were but few bodies known with which they could be naturally connected, the ammonia-bases not having been discovered till afterwards; consequently they did not at the time excite the attention which they really deserved.

A few years later Cahours and Hofmann (Compt. rend. xli. 831; Chem. Gaz. 1855, p. 11), by a similar mode of proceeding with phosphide of sodium and iodide of methyl, obtained the compounds $(CH^3)^2P$, $(CH^3)^3P$ and $(CH^3)^4PI$, the latter being a crystalline compound analogous to iodide of tetramethylammonium; and Berlé (J. pr. Chem. lxvi. 78), by acting upon phosphide of sodium with iodide of ethyl, obtained the compound $(C^2H^5)^3P$ as a yellow strongly fuming liquid, which when heated with iodide of ethyl yielded the crystalline iodide $(C^2H^5)^4PI$. But this mode of preparing the phosphorus-bases is also difficult and dangerous, inflammable and detonating compounds being formed, and complex products obtained, which are very difficult to separate.

The phosphorus-bases containing 1 and 2 atoms of alcohol-radicle are but little known, as no method of obtaining them in a pure state has yet been discovered; but those derived from phosphine, $H^3P$, by the substitution of 3 atoms of alcohol-radicle for 3 atoms of hydrogen, may be obtained pure and in any required quantity by subjecting the zinc-compounds of the alcohol-radicles to the action of trichloride of phosphorus in an atmosphere of carbonic anhydride. Zinc-ethyl, for example, treated in this manner yields chloride of zinc and triethylphosphine:

$$2PCl^3 + 3Zn''(C^2H^5)^2 = 3Zn''Cl^2 + 2(C^2H^5)^3P.$$

The triethylphosphine remains combined with the chloride of zinc, but may be liberated by distillation with aqueous potash, which converts the chloride of zinc into chloride and zincate of potassium:

$$3Zn''Cl^2.2(C^2H^5)^3P + 12KHO = 2(C^2H^5)^3P + 3K^2Zn''O^2 + 6KCl + 6H^2O.$$

Triethylphosphine and trimethylphosphine (the only two compounds of this type hitherto examined) are volatile strongly alkaline liquids, which unite readily with acids, forming crystallisable and for the most part very soluble salts. When treated with the *iodides* of *monatomic alcohol-radicles*, they yield crystalline iodides of monophosphoniums, of the type $R^4PI$, analogous to iodide of tetrethylammonium; and these iodides, when decomposed by moist oxide of silver and by silver-salts, yield the hydrates and salts of the corresponding monophosphoniums; *e. g.* triethylphosphine treated with iodide of ethyl yields iodide of methyl-triethylphosphonium $(CH^3)(C^2H^5)^3PI$, which is converted by moist oxide of silver into the hydrate, $\left.\begin{matrix}(CH^3)(C^2H^5)^3P\\ H\end{matrix}\right\}O$; by nitrate of silver into the nitrate of methyl-triethylphosphonium, $(CH^3)(C^2H^5)^3P.NO^3$, &c.

Numerous compounds belonging to these types have been prepared and examined by Hofmann and Cahours (Phil. Trans. 1857, p. 583; Chem. Soc. Qu. J. xi. 56; Ann. Ch. Pharm. civ.); and further by Hofmann (Phil. Trans.; Chem. Soc. Qu. J. xiii. 289; Ann. Ch. Pharm. Suppl. i. 2).

Triethylphosphine and trimethylphosphine unite with *diatomic alcoholic bromides*, *chlorides*, &c., in the proportion of 1 or 2 at. of the phosphorus-base to 1 at. of the diatomic ether; thus triethylphosphine forms with *bromide of ethylene*, the two compounds $\left.\begin{matrix}(C^2H^4)''Br^2\\(C^2H^5)^3P\end{matrix}\right\}$ and $\left.\begin{matrix}C^2H^4Br^2\\(C^2H^5)^6P^2\end{matrix}\right\}$. From the alcoholic solution of the latter of these compounds, the whole of the bromine is removable by nitrate of silver, whereas from the former only half the bromine can be thus removed. Hence Hofmann regards the latter compound as dibromide of ethylene-hexethyl-diphosphonium, $\left[(C^2H^4)''\begin{matrix}(C^2H^5)^3P\\(C^2H^5)^3P\end{matrix}\right]''Br^2$; the former as bromide of bromethyl-triethylphosphonium $[(C^2H^4Br)(C^2H^5)^3P]Br$; *i. e.* as bromide of tetrethylphosphonium in which 1 at. hydrogen is replaced by bromine. (See AMMONIUM-BASES, i. 197; also ETHYLENE-BASES, ii. 593.)

The last-mentioned compound is susceptible of several remarkable transformations. —*a.* It is resolved by *heat* into hydrobromic acid and bromide of vinyl-triethylphosphonium, $[(C^2H^3)(C^2H^5)^3P]Br$.

*β.* When treated in dilute solution with *hydrate of silver*, it gives up all its bromine and is converted into the compound $\left.\begin{matrix}(C^2H^4)''H^2O^2\\(C^2H^5)^3P\end{matrix}\right\}$, or hydrate of oxethyl-triethylphosphonium, $\left.\begin{matrix}(C^2H^4O)(C^2H^5)^3P\\H\end{matrix}\right\}O$, the change consisting in the replacement of the bromine by an equivalent quantity of peroxide of hydrogen.

*γ.* By boiling for some time with *acetate of silver*, it is converted into acetate of vinyl-triethylphosphonium:

$$[(C^2H^4Br)(C^2H^5)^3P]Br + 2AgC^2H^3O^2 = [(C^2H^3)(C^2H^5)^3P]C^2H^3O^2 + C^2H^4O^2 + 2AgBr.$$

*δ.* It unites:—*a.* With 1 at. *triethyl-* or *trimethyl-phosphine*, forming dibromide of ethylene-hexethyl-diphosphonium, $[(C^2H^4)''(C^2H^5)^6P^2]''Br^2$, and ethylene-triethyl-trimethyl-diphosphonium, $[(C^2H^4)''(C^2H^5)^3(CH^3)^3P^2]''Br^2$.

*b.* With 1 at. *ammonia, ethylamine, methylamine, diethylamine*, &c., forming the dibromides of ethylene-triethyl-phosphammonium, $[(C^2H^4)''(C^2H^5)^3H^3PN]Br^2$; ethylene-tetrethyl-phosphammonium $[(C^2H^4)''(C^2H^5)^4H^2PN]''Br^2$; ethylene-triethyl-methyl-phosphammonium, $[(C^2H^4)''(C^2H^5)^3(CH^3)H^2PN]Br^2$; ethylene-pentethyl-phosphammonium, $[(C^2H^4)''(C^2H^5)^5HPN]''Br^2$, &c.

*c.* With *triethylarsine*, $(C^2H^5)^3As$, yielding dibromide of ethylene-hexethyl-phospharsonium, $[(C^2H^4)''(C^2H^5)^6PAs]''Br^2$.

Trimethylphosphine is acted upon in a similar manner by dibromide of ethylene, yielding the compounds $\left.\begin{matrix}C^2H^4Br^2\\(CH^3)^3P\end{matrix}\right\}$ and $\left.\begin{matrix}C^2H^4Br^2\\(CH^3)^6P^2\end{matrix}\right\}$, from which similar derivatives may be obtained.

All these compounds have been discovered and investigated by Hofmann (Phil. Trans. 1860, pp. 449, 497; Chem. Soc. Qu. J. xiv. 73, 316; Ann. Ch. Pharm. Suppl. i. 2, 145, 177, 306).

The dibromides of methylene, tritylene, tetrylene, amylene, and benzylene likewise react in a similar manner with triethylphosphine, but the resulting compounds are difficult to separate, and have not been much examined.

Lastly, a triphosphonium-compound, namely, tri-iodide of formyl-ennethyl-phosphonium $[(CH)'''(C^2H^5)^9P^3]'''I^3$, is produced by the action of iodoform on triethylphosphine. (Hofmann, Proc. Roy. Soc. x. 189; xi. 290.)

## I. MONOPHOSPHINES AND MONOPHOSPHONIUMS.

### *a. Methyl-compounds.*

**Trimethylphosphine,** $(CH^3)^3P$.—This base is produced by the action of trichloride of phosphorus on zinc-methyl, the process being conducted in the manner to be hereafter described for the preparation of triethylphosphine (p. 609). As the base is extremely volatile, the stream of hydrogen in which it is distilled must be very slow, and the receiver must be kept at a low temperature.

Trimethylphosphine is a transparent, colourless, mobile liquid, heavier than water, having a strong refracting power, and an indescribably nauseous odour, and boiling between 40° and 42°. It is insoluble in water. Its solution in hydrochloric acid yields, with *chloride of platinum*, an orange-yellow indistinctly crystalline precipitate, $2(CH^3)^3HPCl.PtCl^4$, which is easily decomposed at 100°.

Trimethylphosphine, like the corresponding arsines and stibines (i. 340, 398), unites with 2 at. of a monatomic element, Cl, Br, &c., and with 1 at. of a diatomic element, O, S, &c.

The *oxide*, $(CH^3)^3PO$, is produced:—1. By the direct oxidation of trimethylphosphine. This substance has a very powerful attraction for oxygen, fuming and sometimes taking fire in contact with the air. On distilling it, even when recently prepared, the neck of the retort becomes covered in the last stage of the operation, with a beautiful network of crystals of the oxide; they may readily be obtained in larger quantity by exposing the base to a slow current of dry air.—2. By the action of heat on the hydrate of tetramethylphosphonium, marsh-gas being given off at the same time.

$$(CH^3)^4PHO \quad = \quad (CH^3)^3PO \quad + \quad CH^4.$$

The *selenide*, $(CH^3)^3PSe$, obtained by the action of selenium on trimethylphosphine, crystallises like the ethyl-compound (p. 613), melts at 84°. In contact with the air it blackens, with separation of selenium, and gives off the odour of mesitilene (iii. 930).

The *sulphide*, $(CH^3)^3PS$, is obtained by gradually adding flowers of sulphur to an ethereal solution of trimethylphosphine, or by distilling trimethylphosphine with cinnabar. It is not produced by treating the oxide with sulphydric acid or sulphide of ammonium. Crystallises from a highly concentrated aqueous solution in masses of well-formed four-sided prisms, which melt at 105°. (Hofmann and Cahours.)

**Tetramethylphosphonium,** $(CH^3)^4P$.—This base, like all others formed on the ammonium-type, is not known in the free state.

The *iodide*, $(CH^3)^4PI$, is obtained by the action of iodide of methyl on an ethereal solution of trimethylphosphine. It is a white crystalline mass which, when recently prepared, exhibits the silvery lustre of sublimed naphthalene, and assumes a slightly reddish colour in contact with the air. Treated with oxide of silver, and water it yields a very caustic solution of *hydrate of tetramethylphosphonium*.

The *gold-salt*, $(CH^3)^4PCl.AuCl^3$.—Obtained by mixing the solution of chloride of tetramethylphosphonium and trichloride of gold, crystallises from boiling water in brilliant yellow needles.

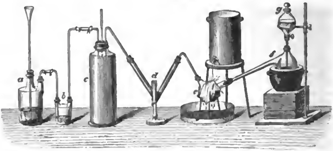
*Platinum-salt*, $2(CH^3)^4PCl.PtCl^4$.—The solution of the oxide mixed with hydrochloric acid and tetrachloride of platinum, yields a platinum-salt, which is insoluble in alcohol and ether, but crystallises from water in beautiful octahedrons. (Hofmann and Cahours.)

### β. *Ethyl-compounds.*

**Triethylphosphine.** $C^6H^{15}P = (C^2H^5)^3P$.—*Formation.* 1. By the action of trichloride of phosphorus on zinc-ethyl (Hofmann and Cahours, p. 607).—2. By the action of phosphide of sodium on iodide of ethyl (Berlé, p. 607).—3. Crystalline phosphide of zinc heated with iodide of ethyl in a sealed tube to 170°—180°, yields zinc-iodide of tetrethylphosphonium, $2(C^2H^5)^4PI.Zn''I^2$, which, when distilled with potash, yields triethylphosphine (Cahours, Ann. Ch. Pharm. cxii. 228; cxxii. 192; Jahresb. 1859, p. 432; 1861, p. 557).—4. When a mixture of zinc, phosphorus, and dry ethylic iodide is heated in a sealed tube to 150°—160°, there is produced, together with zinc-ethyl, a mixture of iodozincate of triethylphosphonium, $2(C^2H^5)^3HPI.Zn''I^2$, iodozincate of tetrethylphosphonium, $2(C^2H^5)^4PI.Zn''I^2$, and a compound of zinc-iodide with oxide of triethylphosphine, $(C^2H^5)^6P^2O.Zn''I^2$. These compounds are separated by their different degrees of solubility in water, the first-mentioned being the least and the second the most soluble. The first yields triethylphosphine when treated with potash in the cold; the third yields it when heated with solid potash; while the second does not yield it when treated with potash either in the cold or with aid of heat. (Hofmann, Chem. Soc. Qu. J. xiii. 291.)

*Preparation.*—A tubulated retort *f* is joined to a receiver *e* (*fig.* 738) which in its turn is connected with a wide glass tube *d*, bent at an angle of about 130° and acting like a second receiver. The angle of this tube is filled with trichloride of phosphorus, and the tube is connected with a large cylinder *c*, which is supplied by a suitable apparatus, *a*, *b*, with dry carbonic anhydride. As soon as the carbonic anhydride has expelled the air from the reservoir, tube, receiver, and retort, an exit-tube from the reservoir, up to that time closed by a caoutchouc cap, is opened to let out the carbonic anhydride, the evolution of which is maintained during the whole operation. The tubulature of the retort is now connected with the copper digester in which the zinc-ethyl has been prepared; and as soon as the retort has received a charge of the ethereal solution of zinc-ethyl, there is fixed into the same tubulature a dropping apparatus, consisting of a glass globe *g*, with a tubulature and stopper at the top, and terminating below in a glass tube in which a stopcock is fitted. This apparatus is filled with trichloride of phosphorus, and by appropriately adjusting the stopcock and opening or closing the stopper of the glass globe, any desired flow of the liquid can be maintained with the greatest nicety. However slowly the trichloride may be added, and however well, moreover, the retort and receiver may be cooled by water or ice, the action is nevertheless so violent, that all the ether, and with it a large quantity of the zinc-ethyl, passes over into the receiver. By the powerful ebullition which periodically ensues, a portion of the vapour is driven even into the bent tube, and a considerable loss of zinc-ethyl is incurred, unless this tube is filled with trichloride of phosphorus,

*Fig.* 738.



which greedily absorbs every trace of the former compound. This fluid valve, ascending and descending in the tube, in accordance with the progress of the reaction, regulates the function of the apparatus so perfectly, that the operation, which always takes several hours, continues by itself when once begun. Sometimes the absorption is so violent that the trichloride of phosphorus in the tube is sucked back into the receiver, but even then no loss is to be feared, since the tube is connected with the reservoir filled with carbonic anhydride. The first drops of trichloride of phosphorus which fall into the solution of zinc-ethyl, hiss like water when coming in contact with red-hot iron. The action becomes by and by less violent, and as soon as an evolution of heat is no longer perceptible, the operation is terminated. There remain in the retort, in the receiver, in the bent tube, and sometimes even in the carbonic acid reservoir, two liquid layers,—the one a heavy, pale straw-coloured, thick liquid, the other a transparent, colourless, mobile liquid floating on the former.

The upper liquid is a mixture of ether and trichloride of phosphorus; the lower, which usually solidifies on cooling, is a compound of triethylphosphine with chloride of zinc, and from this, after the upper layer has been decanted, the phosphorus-base may be separated by distillation with potash. For this purpose it is mixed with water, the retort is filled with hydrogen, and strong potash-ley is allowed to flow slowly into it. On distilling the mixture in a slow stream of hydrogen, the triethylphosphine passes with the aqueous vapour, and floats on the condensed water in the receiver. It is separated by a tap-funnel, dried over sticks of potash, and rectified in a stream of dry hydrogen. (Hofmann and Cahours, p. 607; Hofmann, Chem. Soc. Qu. J. xiii. 290.)

*Properties.*—Triethylphosphine is a transparent, colourless, mobile, strongly refracting liquid. Specific gravity, 0·812 at 15°. Boils at 127·5° under a barometric pressure of 0·744 mm. Its odour is penetrating, almost benumbing, but still not disagreeable, and in a diluted state, resembles that of the hyacinth. Long-continued working with this substance produces head-ache and sleeplessness. When recently prepared, it is without action on vegetable colours, but if exposed to the air for a few seconds, it shows a constantly increasing acid reaction.

*Reactions.*—1. Triethylphosphine is quite insoluble in *water*, but dissolves in all proportions in *alcohol* and *ether*.—2. It unites slowly with *acids*, forming mostly crystallisable, but extremely soluble and deliquescent salts, which may be regarded as salts of triethylphosphonium: *e.g.* $(C^2H^5)^3P.HCl = (C^2H^5)^3HP.Cl$.

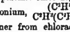
3. Triethylphosphine rapidly absorbs *oxygen* from the air, and is converted into the oxide, $(C^2H^5)^3PO$. In pure oxygen gas it often takes fire and decomposes, emitting dense white fumes of phosphoric anhydride. A mixture of oxygen gas and vapour of triethylphosphine explodes with violence when heated.

4. With *sulphur* and *selenium*, triethylphosphine unites directly, forming the crystalline compounds, $(C^2H^5)^3PS$ and $(C^2H^5)^3PSe$; also with *sulphide of carbon*, forming beautiful red crystals of the compound $2(C^2H^5)^3P.CS^2$. The formation of this compound takes place so readily that triethylphosphine and sulphide of carbon act as extremely delicate tests one for the other. Thus, if a liquid containing free triethylphosphine (or trimethylphosphine) be poured into a watch-glass, and the vapour of the carbonic sulphide allowed to flow upon it from an inclined bottle, the watch-glass soon becomes covered with a beautiful network of the red crystals. If the phosphorus-base is present in the form of a salt, it must first be liberated by adding a drop of potash.

Conversely, triethylphosphine may be very advantageously used for detecting small quantities of carbonic sulphide, as in the most volatile fractions of coal-tar naphtha, and in coal-gas (i. 777).

5. When triethylphosphine is poured into a flask containing *chlorine*, every drop takes fire, with formation of hydrochloric acid and phosphoric chloride, and separation of charcoal. If however the action be moderated, crystalline compounds are formed. It also unites directly with *iodine* and *bromine*, the combination being attended with great evolution of heat and sometimes with inflammation.—6. In *cyanogen gas* it solidifies to a brown resin.

7. *Dibromide of ethylene* and its isomer, *bromide of bromethyl*, unite with 1 at. triethylphosphine, forming bromide of bromethyl-triethylphosphonium, $[(C^2H^4Br)(C^2H^5)^3P]Br$, and with 2 at. triethylphosphine forming dibromide of ethylene-hexethyldiphosphonium, $[(C^2H^4)''(C^2H^5)^6P^2]''Br^2$.—8. *Dichloride of ethylene* and *monochlorinated chloride of ethyl* act in a similar manner.—9. *Di-iodide of ethylene* however acts in a different manner. When brought into contact with dry triethylphosphine, it forms, generally with explosion, ethylene gas and iodide of triethylphosphine, and with alcoholic triethylphosphine it forms a crystalline mass generally consisting of hydriodate of triethylphosphine.

10. When triethylphosphine is heated with *ethylic chloracetate*, $C^2H^2(C^2H^5)ClO^2$, mixed with an equal volume of common ether to moderate the action, a sticky mass is formed, which on addition of platinic chloride, forms the crystallisable chloroplatinate of triethyl-oxethacetylphosphonium,  $\left.\begin{matrix}(C^2H^5)^3\\ C^2H^2(C^2H^5O)'O\end{matrix}\right\}N$, analogous to the ammonium-base produced in like manner from chloracetic ether and triethylamine (ii. 563). (Hofmann, Proc. Roy. Soc. xi. 525.)

Triethylphosphine unites with *sulphocyanate of allyl* (volatile oil of mustard), forming allyl-triethyl-sulphocarbophosphamide, $\left.\begin{matrix}(CS)''\\ C^3H^5\\ (C^2H^5)^3\end{matrix}\right\}\begin{matrix}N\\ P\end{matrix}$; and with *sulphocyanate of phenyl*, forming the analogous phenyl-compound. The *sulphocyanates of methyl, ethyl, amyl* and *ethylene*, on the contrary, do not unite directly with triethylphosphine, but undergo decomposition, yielding sulphide of triethylphosphine and a cyanide of a phosphonium. With *sulphocyanate of ethyl*, for example, the reaction is,

$$(C^2H^5)CNS + 2(C^2H^5)^3P = (C^2H^5)^3PS + [(C^2H^5)^4P]CN;$$

and with *sulphocyanate of ethylene:*

$$(C^2H^4)''C^2N^2S^2 + 4(C^2H^5)^3P = 2(C^2H^5)^3PS + [(C^2H^4)''(C^2H^5)^6P^2]''C^2N^2.$$

11. The *alcoholic cyanates*, on the other hand—the cyanates of ethyl and phenyl for example—neither combine with triethylphosphine, nor are decomposed by it, but merely undergo a molecular transformation, being converted by contact with it into crystalline cyanurates. *Cyanic acid vapour* passed through triethylphosphine yields a white deposit of cyanuric acid.

12. Triethylphosphine and *mercaptan* mixed together in an atmosphere of carbonic anhydride, do not act on one another even at 100°; but if air has access to the mixture, crystals of sulphide of triethylphosphine are gradually formed, the result being due to the oxidation of the triethylphosphine at the expense of atmospheric oxygen, and the subsequent conversion of the oxide into sulphide, according to the equation:

$$(C^2H^5)^3PO + C^2H^6S = C^2H^6O + (C^2H^5)^3PS.$$

It is only, however, at the instant of formation of the oxide that this reaction takes place; for ready formed oxide of triethylphosphine and mercaptan brought together under the most varying conditions of pressure and temperature do not yield a trace of sulphide of triethylphosphine.

13. *Sulphide of nitrogen* (p. 109) is decomposed by triethylphosphine, gas being evolved, and a yellowish liquid formed, which on cooling solidifies to a fibrous mass of crystals of sulphide of triethylphosphine.

### *Compounds of Triethylphosphine.*

**CHLORIDE, BROMIDE, AND IODIDE OF TRIETHYLPHOSPHINE.**—Oxide of triethylphosphine when treated with hydrochloric, hydrobromic and hydriodic acids, is converted into the corresponding chloride, bromide, and iodide, $(C^2H^5)^3PCl^2$, &c., which closely resemble the oxide in their general properties. They are liquids which gradually solidify in the exsiccator; the crystals fuse at 100° and begin to volatilise, although their boiling point is very high. The compounds of triethylphosphine with chlorine, bromine, and iodine may also be obtained by the action of these elements in aqueous or alcoholic solutions upon the phosphorus-base itself. Both methods, however, furnish products which are difficult to purify.

Triethylphosphine forms crystalline compounds with *hydrochloric*, *hydrobromic*, *hydriodic*, *sulphuric* and *nitric acids*; but they can be obtained in the dry state only by means of the exsiccator.

*Chloroplatinate*, $2[(C^2H^5)^3P.HCl].Pt^{iv}Cl^4$.—The solution of the base in hydrochloric acid forms with platinic chloride a crystalline double salt, which is sparingly soluble in cold water, insoluble in alcohol and ether.

*Iodozincate*, $2[(C^2H^5)^3P.HI.].Zn''I^2$.—The product formed by heating dry iodide of ethyl with zinc and phosphorus to 150°—160° for several hours (p. 609), forms with warm water a solution which when left to evaporate deposits an oil which crystallises on cooling (p. 609); and by repeatedly crystallising this product from hot water and alcohol, the iodozincate is obtained in large white crystals which give off triethylphosphine when treated with potash even in the cold (Hofmann). When crystallised phosphide of zinc is heated for some time with iodide of ethyl to 170°—180°, and the product is exhausted with alcohol, an alcoholic solution is obtained, which, when left to evaporate very slowly, deposits, together with iodide of tetrethylphosphonium, beautiful tablets of the iodozincate of triethylphosphine. (Cahours.)

**Oxide of Triethylphosphine**, $(C^2H^5)^3PO$.—This compound is produced: 1. By the direct combination of triethylphosphine with free oxygen. The base has, indeed, so strong an affinity for oxygen that it cannot be distilled without oxidation except in an atmosphere of hydrogen. In the preparation of triethylphosphine by the process above described (p. 609), a quantity of the oxide always accumulates in the residues left after distilling the zinc-chloride compound with potash; and these residues may be advantageously used for preparing the oxide. On subjecting them to distillation, part of the oxide distils over with the aqueous vapour, while the rest passes over only in the subsequent dry distillation of the saline residue. The distillate, which is an aqueous solution of the oxide, is concentrated as much as possible over the water-bath, with or without addition of hydrochloric acid, and the oxide of triethylphosphine is separated as a supernatant oily layer by the addition of solid potash. It is dried by leaving it for 24 hours in contact with sticks of potash, and then redistilled, the first portions which are watery, being rejected, and the receiver changed as soon as the distillate begins to solidify.

2. By gently heating triethylphosphine with oxide of mercury or oxide of silver. Considerable evolution of heat then takes place, the metal is reduced, and oxide of triethylphosphine separates in oily drops or sometimes sublimes in radiated crystals. It also separates in oily drops when triethylphosphine is boiled with strong nitric acid, and potash is added to the highly concentrated liquid.

3. By the action of heat on hydrate of tetrethylphosphonium:

$$(C^2H^5)^4P.H.O = (C^2H^5)^3PO + C^2H^6.$$

On subjecting this compound to distillation, water passes over first, then hydride of ethyl is given off with strong intumescence, and at about 200°, oxide of triethylphosphine distils over as a viscid liquid, solidifying in the neck of the retort towards the end of the operation. (Hofmann and Cahours.)

4. By decomposing the chlorozincate of tetrethylphosphonium, $2(C^2H^5)^4PCl.Zn''Cl^2$, with solid potash and a small quantity of water. An oil smelling of triethylphosphine (probably hydrate of tetrethylphosphonium) then collects on the surface of the strong potash-ley, and when subjected to distillation yields the oxide (Pebal, Ann. Ch. Pharm. cxx. 194).—5. By the action of heat on hydrate of oxethyl-triethyl-phosphonium. (Hofmann.)

$$(C^2H^4O)(C^2H^5)^3P.H.O = (C^2H^5)^3PO + C^2H^4 + H^2O.$$

Oxide of triethylphosphine crystallises in white slender needles often several inches long, permanent in dry air, but deliquescing rapidly in moist air. It melts at 44°, and solidifies at the same temperature (Hofmann); melts at 52·9°, and solidifies at 42° (Pebal). Boils at 240°. Vapour-density 4·60 (Hofmann), by calculation (2 vols.) = 4·659. It dissolves in all proportions in *water* and in *alcohol*, but is less soluble in *ether*; on evaporating the aqueous or alcoholic solutions, the oxide separates at first in the liquid form, and does not solidify till every trace of the solvent has been expelled; it is also precipitated as a liquid from the alcoholic solution by ether, and from the aqueous solution by potash. It dissolves readily in *acids*, and is converted by *hydriodic* or *hydrobromic acid* into the iodide of triethylphosphine, $(C^2H^5)^3PI^2$, or the bromide, $(C^2H^5)^3PBr^2$.

Oxide of triethylphosphine forms crystalline compounds with certain metallic salts.

*a.* With *Cupric sulphate*, $3(C^2H^5)^3PO.Cu''SO^4$.—When crystallised cupric sulphate is added to heated oxide of triethylphosphine, part dissolves with deep green colour while another portion is separated as a basic salt. The green solution turns blue on addition of a little water, and when evaporated in vacuo over oil of vitriol, deposits the compound in green four-sided prisms which deliquesce in damp air, yielding needles of oxide of triethylphosphine. The aqueous solution yields crystals of pure cupric sulphate. (Pebal.)

β. With *Trichloride of Gold*.—This salt added to a concentrated solution of the oxide throws down a deep yellow oil which crystallises with difficulty, and is soluble in water and in alcohol. (Hofmann.)

γ. With *Stannous chloride*.—Oily compound which does not crystallise.

δ. With *Iodide of Zinc*, $2(C^2H^5)^3PO.Zn''I^2$.—Separates on mixing the two solutions as a crystalline precipitate, or as an oil which gradually solidifies in the crystalline form; purified by recrystallisation from alcohol. It forms monoclinic crystals exhibiting the combination ∞P∞ . [∞P∞] . oP . ∞P . [P∞] . −P.[*] Ratio of axes $a:b:c = 0{\cdot}9052 : 1 : 1{\cdot}3312$. Angle of inclined axes = 83° 13′; ∞P : ∞P (orthod.) = 95° 18′; ∞P∞ : ∞P = 132° 21′; ∞P∞ : oP = 96° 47′; oP : ∞P = 94° 34′; oP : [P∞] = 124° 24′; ∞P : −P = 154° 8′. Twins occur with oP as combination-face. Lustre fatty on the faces, vitreous on the fracture. Cleavage distinct parallel to oP and ∞P. The crystals melt at 99°.

OXYCHLORIDE OF TRIETHYLPHOSPHINE, $(C^2H^5)^6P^2Cl^2O$.—When dry hydrochloric acid gas is passed over fused oxide of triethylphosphine, shining crystals of the oxychloride are formed which redissolve in excess of the hydrochloric acid. If heat be then applied to drive off the excess of acid, there remains a very deliquescent crystalline mass, soluble in alcohol, insoluble in ether. The solution treated with platinic chloride forms a compound of that salt with oxide and chloride of triethylphosphine, and when treated with iodide of zinc, it generally yields a compound of zinc-iodide with the oxide of triethylphosphine, and only seldom with the oxychloride.

The *platinum-compound*, $3(C^2H^5)^3PO.(C^2H^5)^3PCl^2.Pt^{iv}Cl^4$, separates also immediately in the crystalline form when dry oxide of triethylphosphine is mixed with a saturated alcoholic solution of platinic chloride. By recrystallisation from alcohol, it is obtained in large orange-red, six-sided monoclinic prisms, exhibiting the faces ∞P∞, oP, ∞P, +P∞, +½P. Ratio of axes $a:b:c = 0{\cdot}6308 : 1 : 1{\cdot}5776$. Angle of inclined axes = 73° 42′; ∞P : ∞P (orthod.) = 113° 22′; oP : ∞P∞ = 106° 18′; oP : ∞P = 98° 52′; oP : + P∞ = 110° 12′; ∞P : +P = 160° 3′. Cleavage distinct parallel to +P∞ and ∞P (Phil. Trans. 1860, p. 419).

The *zinc-compound*, $(C^2H^5)^6P^2Cl^2O.Zn''I^2$, forms transparent colourless octahedrons, soluble in water and in alcohol.

SELENIDE OF TRIETHYLPHOSPHINE, $(C^2H^5)^3PSe$.—Prepared, like the sulphide, by the direct combination of triethylphosphine with selenium; the reaction, however, is less powerful than with sulphur.—Crystallises from water as easily as the sulphide, but the solution is apt to undergo partial decomposition when exposed to the air. Even the dry crystals are slowly reddened in the air. Melts at 112°, and is easily volatilised with partial decomposition. (Cahours and Hofmann.)

SULPHIDE OF TRIETHYLPHOSPHINE, $(C^2H^5)^3PS$.—This compound is produced: 1. By the direct combination of triethylphosphine with sulphur. Flowers of sulphur are gradually introduced into an ethereal solution of triethylphosphine till a portion remains undissolved, the liquid effervescing on each addition. The ether is then volatilised, and the residuary mixture of the sulphide and free sulphur treated with boiling water, which dissolves the sulphide and on cooling deposits it in perfectly pure crystals.—2. By distilling triethylphosphine with cinnabar, which is then reduced to mercurous sulphide or to metallic mercury.—3. By the action of triethylphosphine on sulphide of nitrogen (p. 611).—4. By the decomposition of carbosulphide of triethylphosphine with water or silver-oxide.—5. By the action of mercaptan on triethylphosphine in presence of air (p. 611).

By slowly cooling the aqueous solution, the compound is obtained in beautiful white needle-shaped crystals often five or six inches long. These crystals are six-sided prisms with pyramidal summits (system hexagonal), exhibiting the combination ∞P . P, rarely with ∞P2. Length of principal axis = 0·8211. Angle P : P in the terminal edges = 143° 16′; in the lateral edges = 78° 9′; P : ∞P = 129° 4′. They are optically positive, the index of refraction being 1·65 for the extraordinary, and 1·59 for the ordinary ray (Phil. Trans. 1860, p. 423). The compound melts at 94°, and resolidifies at 88°. When heated beyond 100°, it is volatilised and diffuses a white vapour having a disagreeable sulphur odour, which is but slightly perceptible at common temperatures. When heated with a quantity of water not sufficient for its solution, it rises to the surface in the form of a transparent oil which is copiously volatilised with the aqueous vapour.

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[*] The crystalline forms and optical properties of this and the other compounds of the phosphorus-bases, as determined by Quintino Sella, are fully described in Hofmann's Memoir (Phil. Trans. 1860, p. 409); also in Sella's Memoir, "*Sulle forme cristalline di alcuni sali derivati dall' ammoniaca*," Torino, 1861 (from the "Memorie della Reale Accademia delle Scienze di Torino" [2] xx.). See also Jahresb. 1860, p. 331 *et seq.*; 1861, p. 467 *et seq.*

Sulphide of triethylphosphine is instantaneously decomposed by *potassium* or *sodium* with separation of triethylphosphine.

It is much more soluble in hot than in cold *water*, only a small quantity remaining dissolved at ordinary temperatures. It is still less soluble in *alkaline liquids*. On adding an alkali to the cold aqueous solution, the mixture becomes turbid and soon deposits small crystals. On adding potash to the boiling saturated aqueous solution, the sulphide instantly separates in oily drops, which, as the liquid cools, rapidly solidify into spherical aggregates of crystals. It dissolves even more readily in *alcohol* and *ether*, and in *disulphide of carbon* almost without limit; from this solvent it does not crystallise perfectly.

The aqueous solution is without action on vegetable colours; the compound nevertheless appears to possess weak basic properties. It dissolves more readily in *hydrochloric acid*, especially when concentrated, than in water, and the solution furnishes with tetrachloride of platinum a yellow precipitate, which however rapidly cakes into a resinous mass, giving indications of decomposition by the separation of platinic sulphide. The sulphide also dissolves in dilute *sulphuric* and *nitric acids;* concentrated nitric acid decomposes it; the fuming acid gives rise to a sort of detonation. The aqueous solution is not affected by *acetate of lead*, *nitrate of silver*, or *mercuric oxide*, even at the boiling temperature; the alcoholic solution, on the other hand, is instantaneously decomposed, with separation of the sulphide of lead, silver, or mercury.

CARBOSULPHIDE OF TRIETHYLPHOSPHINE, $(C^2H^5)^3P.CS^2 = \left.\begin{matrix}(CS)''\\(C^2H^5)^3\end{matrix}\right\}\begin{matrix}P\\S\end{matrix}$. Triethylphosphine and disulphide of carbon combine together with violence, forming a red crystalline mass. On mixing the two substances in alcoholic or ethereal solution, the compound immediately separates in red crystalline laminæ, which may be purified by recrystallisation from alcohol, and dried over oil of vitriol. It forms dark red monoclinic prisms, in which the axes $a : b : c = 1·5970 : 1 : 0·9205$. Angle $b : c$ = 56° 49′. Observed faces $\infty P\infty$, $[\infty P\infty]$, $oP$, $\infty P$, $+P\infty$. Angle $\infty P : \infty P$ (orthod.) = 55° 19′; $oP : \infty P\infty$ = 123° 11′; $oP : \infty P$ = 119° 0′; $oP : +P\infty$ = 122° 47′. Cleavage distinct parallel to $[\infty P\infty]$ and $\infty P\infty$ (Phil. Trans. 1860, p. 428). It melts at 90° and votatilises at 100°. Heated with *water* in a sealed tube to 100° for several days, it is decomposed, with formation of sulphide and oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and carbonic disulphide, the latter being further partly converted by the water into carbonic dioxide and sulphydric acid:

$$4[(C^2H^5)^3P.CS^2] + 2H^2O = 2(C^2H^5)^3PS + (C^2H^5)^3PO + (CH^3)(C^2H^5)^3PHO + 3CS^2.$$

The alcoholic solution boiled with *oxide* or *nitrate of silver* yields sulphide of triethylphosphine together with metallic silver, sulphide of silver, and carbonic dioxide:

$$(C^2H^5)^3P.CS^2 + 2Ag^2O = (C^2H^5)^3PS + Ag^2S + Ag^2 + CO^2.$$

Carbosulphide of triethylphosphine dissolves in strong *hydrochloric acid*, but is precipitated by potash or ammonia without alteration. The acid solution forms with *trichloride of gold* and with *tetrachloride of platinum*, yellow amorphous double salts, which are insoluble in alcohol and ether, change colour and give off hydrochloric acid during drying. The *platinum-salt* = $2[(C^2H^5)^3P.CS^2]\,H^2Cl^2.Pt^{iv}Cl^4$. (Hofmann.)

SULPHOCYANATE OF TRIETHYLPHOSPHONIUM, $(C^2H^5)^3HP.CNS = \left.\begin{matrix}(CS)''\\(C^2H^5)^3\\H\end{matrix}\right\}\begin{matrix}N.\\P\end{matrix}$ Produced by dissolving triethylphosphine in sulphocyanic acid. When heated, it partly volatilises undecomposed, but the greater part suffers decomposition, giving off sulphide and carbo-sulphide of triethylphosphine, together with free carbonic disulphide and leaving a brown ill-defined substance which gives off ammonia when treated with an alkali. (Hofmann.)

**Tetrethylphosphonium**, $(C^2H^5)^4P$.—Known only in combination. The *hydrate*, $\left.\begin{matrix}(C^2H^5)^4P\\H\end{matrix}\right\}O$, is obtained by the action of silver-oxide on the iodide. A strongly alkaline, nearly inodorous bitter liquid is thereby formed, which retains a little silver in solution, and dries up over oil of vitriol to a crystalline, extremely deliquescent mass, the silver separating at the same time as a black powder, or as a brilliant metallic mirror. This mass when redissolved in water yields a colourless liquid free from silver, but generally containing carbonic acid. The solid hydrate absorbs water and carbonic acid with avidity.

In its deportment with other substances, hydrate of tetrethylphosphonium resembles hydrate of tetrethylammonium (ii. 561), its solution reacting with metallic salts,—like a solution of caustic potash; but some of the precipitates, *e. g.* alumina and zinc-oxide, dissolve less readily in excess of the phosphorus-base.

The hydrate is resolved by heat into hydride of ethyl and oxide of triethylphosphine (p. 612). If however it has been exposed for some time to the air and has absorbed carbonic acid, a different decomposition takes place, the carbonate of tetrethylphosphonium being resolved into triethylphosphine and carbonate of ethyl, which passes over in the form of an inflammable aromatic liquid, without any evolution of permanent gas:

$$[(C^2H^5)^4P]^2CO^3 \quad = \quad 2(C^2H^5)^3P \quad + \quad (C^2H^5)^2CO^3.$$

Salts of Tetrethylphosphonium.—The hydrate dissolves in hydrochloric, nitric and sulphuric acids, forming crystallisable deliquescent salts, soluble in alcohol but for the most part insoluble in ether. The *hydrochlorate* forms sparingly soluble precipitates with trichloride of gold and tetrachloride of platinum. The *gold-salt*, $(C^2H^5)^4P.AuCl^3$, crystallises from boiling water in shining yellow needles. The *platinum-salt*, $2(C^2H^5)^4P.PtCl^4$, is a pale orange-yellow precipitate, sparingly soluble in boiling water, insoluble in alcohol and ether, not decomposing at 100°. When recrystallised from boiling water, it forms regular octahedrons having their summits replaced by faces of the cube.

*Chlorozincate*, $2(C^2H^5)^4PCl.Zn''Cl^2$.—When oxychloride of phosphorus is added by drops to pure zinc-ethyl, a violent reaction is set up (explosive if an ethereal solution of zinc-ethyl is used), and a colourless syrup is formed which gradually solidifies to a vitreous mass, which is decomposed by water into gaseous hydride of ethyl, insoluble oxychloride of zinc, and a solution which when evaporated over oil of vitriol yields the chlorozincate in colourless transparent dimetric crystals:

$$4Zn''(C^2H^4)^2 \ + \ 2POCl^3 \ = \ 2(C^2H^4)^4PCl.Zn''Cl^2 \ + \ 2Zn''O \ + \ Zn''Cl^2.$$

The double salt is permanent in the air and easily soluble in water. (Pebal, Ann. Ch. Pharm. cxx. 198.)

*Iodide*, $(C^2H^5)^4PI$.—On mixing triethylphosphine with iodide of ethyl, a violent action ensues after a few moments, the liquid effervescing with almost explosive violence, and then solidifying in a white crystalline mass. If an ethereal solution of triethylphosphine is used, the crystals form more slowly. It is also produced by submitting hydrate of ethylene-hexethyl-diphosphonium (p. 621) to the action of heat, and neutralising the alkaline residue (which contains hydrate of tetrethylphosphonium) with hydriodic acid.

Iodide of tetrethylphosphonium crystallises in rhombohedral combinations (more or less complex according to the mode of preparation) of the faces oR, $\infty P2$, R, $-\frac{1}{2}R$, $\frac{4}{3}P2$. The angles of these several faces in the terminal edges are as follows: R : R = 83° 26′; $\frac{4}{3}P2 : \frac{4}{3}P2$ = 127° 5′; $\frac{4}{3}P2 : \frac{4}{3}P2$ = 139°; $-\frac{1}{2}R : -\frac{1}{2}R$ = 111° 46′; R : oR = 120° 28′; oR : $\frac{4}{3}P2$ = 117°. Isomorphous with iodide of silver. (Phil. Trans. 1860, p. 533; Jahresb. 1861, p. 478.)

The iodide is very soluble in water, less soluble in alcohol, insoluble in ether. The aqueous solution crystallises on addition of potash-solution, in which this compound, like the iodides of tetramethylammonium and tetrethylammonium (ii. 562; iii. 999), is but slightly soluble. From the alcoholic solution it is deposited on addition of ether, as a crystalline powder. If ether be added to a cold alcoholic solution, as long as the precipitate first formed is dissolved by boiling, well-formed crystals of the iodide are deposited on cooling.

*Iodozincate*, $2(C^2H^5)^4PI.Zn''I^2$.—This salt, which constitutes the chief product of the action of ethylic iodide on crystallised phosphide of zinc (p. 609), forms beautiful yellowish crystals. (Cahours.)

**Methyl-triethylphosphonium,** $(CH^3)(C^2H^5)^3P$.—The *iodide*, $(CH^3)(C^2H^5)^3PI$, is produced by direct combination of methylic iodide with triethylphosphine. The *hydrate* is obtained by treating the iodide with silver-hydrate, or by heating carbosulphide of triethylphosphine with water (p. 614). The aqueous solution mixed with hydrochloric acid and tetrachloride of platinum yields the *platinum-salt*, $2(CH^3)(C^2H^5)^3PCl.PtCl^4$.

**Ethyl-trimethylphosphonium,** $(C^2H^4)(CH^3)^3P$.—The *iodide*, $(C^2H^5)(CH^3)^3PI$, is obtained by adding iodide of ethyl to an ethereal solution of trimethylphosphine, and purified by recrystallisation from boiling water. The *hydrate*, obtained by decomposing the silver-salt with silver-hydrate, yields with hydrochloric acid and tetrachloride of platinum a *platinum-salt*, $2(C^2H^5)(CH^3)^3PCl.PtCl^4$, crystallising in large well-defined octahedrons.

### γ. *Amyl-compounds.*

**Trimethylamylphosphonium,** $C^8H^{20}P = (CH^3)^3(C^5H^{11})P$.—The *iodide*, $C^8H^{20}PI$, is deposited slowly from an ethereal mixture of iodide of amyl and trimethylphosphine. It is extremely soluble in water, so that if the ethereal solution of iodide of amyl contains only a trace of water, the salt separates in the form of a syrup which only gradually solidifies. From absolute alcohol it crystallises, though with difficulty, in needles.

*Chloroplatinate*, $2(CH^3)^3(C^5H^{11})PCl.PtCl^4$.—The hydrate, formed from the iodide by means of hydrate of silver, yields with hydrochloric acid and tetrachloride of platinum a very soluble platinum-salt, which crystallises from boiling water in splendid needles aggregated in spherules. (Hofmann and Cahours.)

**Triethylamylphosphonium,** $C^{11}H^{26}P = (C^2H^5)^3(C^5H^{11})P$.—Iodide of amyl acts but slowly on triethylphosphine. An ethereal mixture of the two substances deposits in a few days beautiful crystals of the *iodide* $C^{11}H^{26}PI$, which may be purified by solution in alcohol and precipitation by ether.

The *hydrate*, obtained by treating the iodide with hydrate of silver, resembles the hydrate of tetrethylphosphonium. When heated, it gives off a small quantity of inflammable gas, probably hydride of ethyl, a liquid being also formed, which boils at about 280°, and appears to be the oxide of diethylamylphosphine:

$$(C^2H^5)^3(C^5H^{11})PHO = (C^2H^5)^2(C^5H^{11})PO + C^2H^5.H.$$

*Chloroplatinate*, $2(C^2H^5)^3(C^5H^{11})PCl.PtCl^4$.—The solution of the hydrate in hydrochloric acid, deposits, on addition of tetrachloride of platinum, a beautiful platinum-salt, which crystallises in prisms with flat terminal planes. It is insoluble in alcohol and ether, but rather soluble in water,

### δ. *Allyl-compounds.*

**Triethyl-allylphosphonium,** $C^9H^{20}P = (C^2H^5)^3(C^3H^5)P$.—Iodide of allyl acts with great energy on triethylphosphine, forming a solid product which, when recrystallised from alcohol, yields splendid needles of the *iodide*, $(C^2H^5)^3(C^3H^5)PI$. The *chloride* and *hydrate* resemble the corresponding compounds of tetrethylphosphonium. The *chloroplatinate* crystallises readily in octahedrons. The *sulphocyanate*, $(C^2H^5)^3(C^3H^5)P.CNS$, obtained by treating the hydrate with sulphocyanic acid, is easily soluble and crystallises with difficulty. (Hofmann, Phil. Trans. 1860, 442.)

**Triethyl-allyl-sulphocarbo-phosphonitride,** $C^{10}H^{20}NPS + \left.\begin{matrix}(CS)\\(C^2H^5)^3\\C^3H^5\end{matrix}\right\}\begin{matrix}N\\P\end{matrix}.$ (Hofmann, Phil. Trans. 1860, p. 439).—This base, metameric with the sulphocyanate just mentioned, and formed on the carbamide or urea type, is produced by the direct combination of 1 at. sulphocyanate of allyl with 1 at. triethylphosphine. The two bodies act on one another with great violence, forming a brown mixture which, after some days, yields brown crystals difficult to purify. It is better to mix the two substances in ethereal solution, a crystalline mass being then obtained, which may be purified by washing it with cold ether, and once recrystallising from boiling ether.

This compound crystallises with great facility in colourless, transparent, well-defined crystals, half an inch long. They are monoclinic, exhibiting the faces ∞P∞, oP, ∞P, +P∞, +2P∞, $+\frac{1}{2}$P. Ratio of axes, $a : b : c = 0{\cdot}8321 : 1 : 0{\cdot}3984$. Angle of inclined axes, $b, c = 115° 15'$. Angle ∞P : ∞P (orthod.) = 132° 27; oP : ∞P = 99° 45′; oP : ∞P∞ = 115° 15′; oP : +P∞ = 130° 26′; oP : + 2P∞ = 100° 54′. The crystals are less hard than gypsum; cleave easily and distinctly parallel to ∞P∞ and oP. (Phil. Trans. 1860, 440.)

The compound is insoluble in water, but easily soluble in alcohol, the solution having a faint alkaline reaction. It melts at 68°, and solidifies at 61°. At a higher temperature it decomposes, emitting a peculiarly repulsive odour, and yielding crystals of sulphide of triethylphosphine in considerable quantity. It dissolves readily in hydrochloric acid, and the solution mixed with platinic chloride yields a light yellow scaly precipitate of a *platinum-salt*,

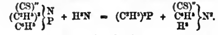
$$C^{20}H^{42}N^2P^2S^2PtCl^6 = 2[(CS)''(C^2H^5)^3(C^3H^5)NP].H^2Cl^2.Pt^{iv}Cl^4.$$

### ε. *Phenyl-compound.*

**Triethyl-phenyl-sulphocarbo-phosphonitride,** $C^{13}H^{20}NPS = \left.\begin{matrix}(CS)''\\(C^2H^5)^3\\C^6H^5\end{matrix}\right\}\begin{matrix}N\\P\end{matrix}$ (Hofmann, Phil. Trans. 1860, p. 432).—This base, analogous in composition to the allyl-compound just described, is produced in like manner by the direct combination of triethylphosphine with sulphocyanate of phenyl, and likewise purified by washing with cold ether and crystallisation from boiling ether. The crystals are monoclinic, exhibiting the faces ∞P, ∞P∞, (∞P∞), oP, with the angles ∞P : ∞P (orthod.) = 91° 6′; oP : ∞P′ = 109° 50′; oP′ : ∞P∞ = 118° 58′. The crystals are about as hard as gypsum, and cleave distinctly parallel to ∞P∞, with fibrous cleavage parallel to ∞P∞. This compound is homœomorphous with the preceding, also with thiosinnamine or allyl-sulphocarbamide.

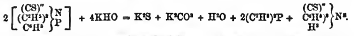
The phenylic phosphonitride melts at 57·5°, and decomposes at 100° like the allyl-compound, emitting also an extremely repulsive odour. The same decomposition takes place gradually at common temperatures, and most quickly when the compound is heated to 150°—160° in sealed tubes.

The phosphonitride is insoluble in *water*, but soluble in *alcohol* and in boiling *ether*. It dissolves also with the greatest facility in *acids*, even when very dilute, forming, in many cases, easily crystallisable salts which are capable of double decomposition, and from which the base may be separated by careful addition of potash or ammonia. They are however very prone to decomposition. *Nitric acid*, even if extremely dilute, decomposes the compound, separating sulphocyanate of phenyl, and converting the triethylphosphine into oxide. The solution of the base in *hydrochloric acid* is more stable, but becomes milky when largely diluted with water, sulphocyanate of phenyl separating out, and chloride of triethylphosphonium remaining in solution. *Ammonia* added to the concentrated hydrochloric solution, separates the base without decomposition; but if the dilute solution be boiled with ammonia, the turbidity perceptible at the commencement disappears again, and after a few moments, crystals of **phenylsulphocarbamide** separate, triethylphosphine being likewise set free:



$$\left.\begin{matrix}(CS)''\\(C^2H^5)^3\\C^6H^5\end{matrix}\right\}\begin{matrix}N\\P\end{matrix} + H^3N = (C^2H^5)^3P + \left.\begin{matrix}(CS)''\\C^6H^5\\H^3\end{matrix}\right\}N^2.$$

*Potash* acts in a similar manner, excepting that it separates **diphenyl-sulphocarbamide**:



$$2\left[\left.\begin{matrix}(CS)''\\(C^2H^5)^3\\C^6H^5\end{matrix}\right\}\begin{matrix}N\\P\end{matrix}\right] + 4KHO = K^2S + K^2CO^3 + H^2O + 2(C^2H^5)^3P + \left.\begin{matrix}(CS)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2.$$

On adding a few drops of *carbonic disulphide* to a solution of the phenylic phosphonitride, the liquid becomes deep red, and on cooling deposits crystals of carbosulphide of triethylphosphine; and the mother-liquor yields, on evaporation, oily drops of phenylic sulphocyanate.

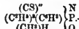
*Hydrochlorate*, $C^{13}H^{20}NPS.HCl$.—The solution of the phosphonitride in hydrochloric acid solidifies on cooling to a crystalline mass, which when recrystallised from moderately warm water, yields splendid cadmium-yellow crystals often an inch long. Boiling water decomposes it, and the dry salt likewise decomposes at 100°. The same is the case with all the other salts of the base: they must therefore be dried in vacuo over oil of vitriol.

The *hydrobromate* is analogous to the hydrochlorate in composition and in properties.

The *chloroplatinate*, $2C^{13}H^{21}NPSCl.PtCl^4$, separates as a light-yellow crystalline precipitate, or from dilute solutions in somewhat better-formed crystals, often in lily-shaped aggregations.

*Methyl-iodide*, $C^{13}H^{20}NPS.CH^3I = \left.\begin{matrix}(CS)''\\(C^2H^5)^3\\C^6H^5\\CH^3\end{matrix}\right\}\begin{matrix}N\\P\\I\end{matrix}$.—This compound is formed on pouring iodide of methyl into an ethereal solution of the phenylic phosphonitride, and separates immediately as a heavy oil which rapidly solidifies into a crystalline mass. It is soluble in boiling water, and separates on cooling in splendid golden-yellow needles.

*Methyl-chloroplatinate*, $C^{28}H^{46}N^2P^2S^2PtCl^6 = 2(C^{13}H^{20}NPS.CH^3Cl).Pt^{iv}Cl^4$.—The chloride obtained by treating the methyl-iodide with chloride of silver, yields on addition of platinic chloride, an acicular platinum-salt having this composition, which may be recrystallised from boiling water.



*Methyl-hydrate*, $C^{14}H^{23}NPSO = C^{13}H^{20}NPS.CH^3(HO) = \left.\begin{matrix}(CS)''\\(C^2H^5)^3(C^6H^5)\\(CH^3)H\end{matrix}\right\}\begin{matrix}N\\P\\O\end{matrix}$.—The iodide treated with moist oxide of silver yields a very caustic alkaline liquid containing this hydrate, inasmuch as, when saturated with hydrochloric acid and mixed with platinic chloride, it yields the acicular platinum-salt just described. It is however easily decomposed; for on boiling, it emits the odour of phenylic sulphocyanate, and if the boiling be prolonged till this odour is no longer perceptible, addition of hydrochloric acid and platinic chloride no longer produces the acicular platinum-salt, but in its place large yellow octahedrons are deposited on evaporation, consisting of the chloroplatinate of methyl-triethyl-phosphonium.

### ζ. *Benzyl-compound.*

**Triethyl-benzyl-phosphonium.** The *chloride*, $(C^2H^5)^3(C^7H^7)PCl$, is produced by heating triethylphosphine with chloride of benzylene, $C^7H^6Cl^2$, to 120°—130°; best in presence of alcohol:

$$3(C^2H^5)^3P + C^7H^6Cl^2 + H^2O = (C^2H^5)^3(C^7H^7)PCl + (C^2H^5)^3HPCl + (C^2H^5)^3PO.$$

The benzyl-phosphonium base, liberated by successive treatment with baryta, oxide of silver, and carbonic acid, forms a strongly alkaline liquid, yielding a well crystallised, but very deliquescent iodide, and a sparingly soluble platinum-salt, which when recrystallised from boiling water, exhibited the composition $2[(C^2H^5)^3(C^7H^7)PCl]PtCl^4$.

### η. *Monophosphoniums produced by the action of Diatomic alcoholic Bromides, Chlorides, &c. on Trimethyl- and Triethyl-phosphine.*

**Bromethyl-triethyl-phosphonium.** $(C^2H^4Br)(C^2H^5)^3P$.—The *bromide* of this radicle, $C^8H^{19}PBr^2 = (C^2H^4Br)(C^2H^5)^3PBr$, is produced, together with dibromide of ethylene-hexethyl-diphosphonium, by the action of dibromide of ethylene on triethylphosphine (pp. 608, 611):

$$(C^2H^5)^3P + C^2H^4Br^2 = (C^2H^4Br)(C^2H^5)^3PBr$$

and

$$2(C^2H^5)^3P + C^2H^4Br^2 = (C^2H^4)''(C^2H^5)^6P^2Br^2.$$

The mixture becomes turbid at first and gradually solidifies to a saline mass of the two salts; the action is accelerated by gentle heating. It is best to add the dibromide of ethylene to triethylphosphine mixed with twice its volume of ether in a flask filled with carbonic dioxide and provided with an upright condensing tube. As soon as the liquid, on being heated with carbonic disulphide (p. 710), gives no further indication of the presence of free triethylphosphine, the separated crystals are collected on a filter and washed with ether to free them from adhering dibromide of ethylene. To separate the two bromides (which are accompanied by small quantities of oxide and hydrobromate of triethylphosphine) they are crystallised three or four times from absolute alcohol, mixed for the last crystallisation with a little ether. The much more soluble diphosphonium-bromide then remains in the mother-liquors, and the bromide of bromethyl-triethyl-phosphonium is ultimately obtained quite pure and sometimes in separate well-developed crystals.—2. Brominated ethylic bromide ($C^2H^4Br.Br$), acts upon triethylphosphine in a similar manner, but less energetically, and yields a smaller proportion of the monophosphonium-bromide.

Bromide of bromethyl-triethyl-phosphonium crystallises in white, unctuous, much elongated rhombic dodecahedrons, very soluble in water and in aqueous *alcohol*, less soluble in absolute alcohol. It melts at 235°, and decomposes at higher temperatures, giving off hydrobromic acid.

*Silver-salts* added to a cold solution of this bromide, throw down only half the bromine, yielding salts of bromethyl-triethylphosphonium which generally form double salts with the excess of the silver-salt. On continued boiling, however, the whole of the bromine is precipitated as bromide of silver, with formation of a salt of vinyl-triethylphosphonium (p. 608). It is on account of the greater force with which one-half of the bromine is retained, that the compound is supposed to contain a brominated radicle. For another view of the constitution of this and similar compounds, see AMMONIUM-BASES (i. 197). *Silver-oxide* digested with bromide of bromethyl-triethylphosphonium, precipitates all the bromine, and forms a solution of hydrate of oxethyl-triethylphosphonium. *Potash* has no action on the compound in the cold; after prolonged boiling it produces reactions which have not yet been examined. When a solution of the bromide, acidulated with *sulphuric acid*, is digested with granulated *zinc*, bromide of tetrethylphosphonium is produced:

$$(C^2H^4Br)(C^2H^5)^3PBr + H^2 = (C^2H^5)^4PBr + HBr.$$

Bromide of bromethyl-triethyl-phosphonium unites with 1 at. *triethyl-* or *trimethyl-phosphine*, forming dibromide of ethylene-hexethyl-diphosphonium or of ethylene-trimethyl-triethyl-diphosphonium; similarly with 1 at. *ammonia*, *ethylamine*, *diethylamine*, and *trimethylamine*, forming dibromides of phosphammoniums: *e.g.*—

$$(C^2H^4Br)(C^2H^5)^3PBr + NH^3 = [(C^2H^4)''(C^2H^5)^3H^3PN]''Br^2.$$

*Triethylamine* alone acts in a different way; in presence of not perfectly dehydrated alcohol, it forms bromide of oxethyl-triethyl-phosphonium and bromide of triethyl-ammonium:

$$(C^2H^4Br)(C^2H^5)^3PBr + (C^2H^5)^3N + H^2O = (C^2H^5O)(C^2H^5)^3PBr + (C^2H^5)^3HNBr.$$

If water be completely excluded, no action takes place at 100°, and the products formed above 130° have not yet been examined.

*Chloride of Bromethyl-triethyl-phosphonium* is obtained by digesting the bromide with chloride of silver. It is very soluble in water and in alcohol, and only imperfectly crystallisable. The *chloro-aurate*, $(C^2H^4Br)(C^2H^5)^3PCl.AuCl^3$, crystallises from boiling water in light yellow needles slightly soluble in cold water. The *chloroplatinate*, $2[(C^2H^4Br)(C^2H^5)^3PCl]PtCl^4$, forms long monoclinic prisms having an orange-yellow colour and vitreous lustre. The crystals are combinations of the faces ∞P∞, [∞P∞], ∞P, +P∞, −P∞, [P∞], +P, −P, 2P2. Angle ∞P : ∞P (orthod.) = 91° 49′; ∞P : +P = 133° 45′; ∞P : −P = 133° 3′; +P∞ : +P = 150° 37′; −P∞ : −P = 150° 14′; 2P2 : −P = 160° 53′; 2P2 : ∞P = 141° 39′ (Phil. Trans. 1860, p. 497). Ratio of axes $a : b : c = 0·9685 : 1 : 0·6580$. Angle of inclined axes $b, c$ = 89° 2′. The salt dissolves rather sparingly in cold, more easily in boiling water, and may be recrystallised without decomposition.

*Iodide of Bromethyl-triethyl-phosphonium*, obtained by decomposing the sulphate with iodide of barium, forms sparingly soluble pearly scales. The *nitrate* is similar to the chloride. The *sulphate* separates in long white needles, easily soluble in water and alcohol, when the bromide is first converted, by treatment with silver-sulphate, into a double sulphate of silver and bromethyl-triethyl-phosphonium, and the solution, after being freed from silver by sulphydric acid and evaporated, is mixed with a little alcohol and ether. (Hofmann.)

**Chlorethyl-triethyl-phosphonium.** $(C^2H^4Cl)(C^2H^5)^3P$.—When triethylphosphine is left in contact for several days at common temperatures with dichloride of ethylene, or with its isomer, monochlorinated ethylic chloride, a white crystalline mass is formed, which contains chloride of chlorethyl-triethyl-phosphonium, together with a large quantity of dichloride of ethylene-hexethyl-diphosphonium. On mixing the aqueous solution with tetrachloride of platinum, a pale yellow crystalline precipitate is first formed consisting of the platinum-salt of the diphosphonium; but this after a few hours becomes covered with deep orange-yellow crystals of the monophosphonium platinum-salt, easily separated from the preceding by mechanical means. The *chloroplatinate*, $2[(C^2H^4Cl)(C^2H^5)^3PCl].PtCl^4$, is more soluble than the corresponding bromethylated salt.

Chloride of chlorethyl-triethylphosphonium is also produced by the action of pentachloride of phosphorus on the chloride of oxethyl-triethylphosphonium:

$$(C^2H^5O)(C^2H^5)^3PCl + PCl^5 = (C^2H^4Cl)(C^2H^5)^3PCl + HCl + POCl^3.$$

**Oxethyl-triethylphosphonium,** $C^8H^{20}PO = (C^2H^5O)(C^2H^5)^3P$.—The *hydrate*, $\left.\begin{matrix}(C^2H^5O)(C^2H^5)^3P\\H\end{matrix}\right\}O$, is obtained by digesting bromide of bromethyl-triethylphosphonium with hydrate of silver:

$$(C^2H^4Br)(C^2H^5)^3PBr + 2AgHO = (C^2H^5O)(C^2H^5)^3PHO + 2AgBr;$$

or by decomposing the sulphate of bromethyl-triethylphosphonium with caustic baryta. When the filtrate obtained in either case is evaporated over oil of vitriol, there remains a very deliquescent syrup from which potash separates the base in oily drops. When strongly heated, it is resolved into oxide of triethylphosphine, ethylene-gas, and water:

$$(C^2H^5O)(C^2H^5)^3PHO = (C^2H^5)^3PO + C^2H^4 + H^2O.$$

The hydrate dissolves easily in acids, forming more or less crystallisable salts.

The *bromide* and *chloride* are indistinctly crystalline, extremely soluble, and easily form double salts with bromide and chloride of zinc. The chloride is violently attacked by pentabromide of phosphorus, and converted into chloride of bromethyl-triethyl-phosphonium:

$$(C^2H^5O)(C^2H^5)^3PCl + PBr^5 = (C^2H^4Br)(C^2H^5)^3PCl + POBr^3 + HBr.$$

The *chloro-aurate*, $(C^2H^5O)(C^2H^5)^3PCl.AuCl^3$, forms gold-yellow needles which dissolve sparingly in boiling water, and melt to a yellow oil when the quantity of water is insufficient to dissolve them.

The *chloroplatinate*, $2[(C^2H^5O)(C^2H^5)^3PCl].PtCl^4$, crystallises on evaporating a solution of the chloride mixed with tetrachloride of platinum, in small orange-yellow, well-developed quadratic octahedrons, in which the angle P : P in the terminal edges

= 70° 7′—71° 4′ (calc. 70° 32′); and in the lateral edges 109° 32′—109° 44′ (calc. 109° 28′) (Phil. Trans. 1860, p. 464). The salt is easily soluble in hot water.

The *iodide*, $(C^2H^5O)(C^2H^5)^3PI$, crystallises from a solution of the hydrate saturated with hydriodic acid, and left to evaporate, in long needles which decompose at 100°.

The *perchlorate* forms laminæ slightly soluble in cold water.

**Vinyl-triethylphosphonium,** $(C^2H^3)(C^2H^5)^3P$.—1. The salts of this base are obtained by prolonged boiling of salts of bromethyl-triethylphosphonium with silver-salts, the acetate being the most easily produced:

$$(C^2H^4Br)(C^2H^5)^3PBr + 2AgC^2H^3O^2 = (C^2H^3)(C^2H^5)^3P.C^2H^3O^2 + C^2H^4O^2 + 2AgBr.$$

2. The hydrate appears to be produced under certain circumstances by the action of heat on hydrate of oxethyl-triethylphosphonium.—3. Bromide of bromethyl-triethylphosphonium is decomposed by prolonged heating, probably into hydrobromic acid and bromide of vinyl-triethylphosphonium.

*Chloroplatinate.*—The solution (1), filtered from bromide of silver, yields, on addition of platinic chloride and sufficient concentration, octahedral crystals of the salt $2(C^2H^3)(C^2H^5)^3PCl.PtCl^4$. (Hofmann.)

**Iodomethyl-triethylphosphonium,** $(CH^2I)(C^2H^5)^3P$.—Triethylphosphine unites directly with di-iodide of methylene $C^2H^2I^2$, forming the iodide $(CH^2I)(C^2H^5)^3PI$, which when treated with hydrate of silver at ordinary temperatures yields the corresponding hydrate $\left.\begin{matrix}(CH^2I)(C^2H^5)^3P\\H\end{matrix}\right\}O$. (Hofmann, Proc. Roy. Soc. x. 613.)

**Chloromethyl-triethylphosphonium.** The *chloride*, $(CH^2Cl)(C^2H^5)^3PCl$, obtained in like manner by the union of 1 at. dichloride of ethylene and 1 at. triethylphosphine, forms with platinic chloride a double salt which crystallises well. The chloride is capable of taking up a second atom of triethylphosphine, and forming the dichloride of methylene-hexethyl-diphosphonium, $(CH^2)''(C^2H^5)^6P^2Cl^2$, which is decomposed by water, yielding chloride of methyl-triethylphosphonium, oxide of triethylphosphine and hydrochloric acid:

$$(CH^2)''(C^2H^5)^6P^2Cl^2 + H^2O = (CH^3)(C^2H^5)^3PCl + (C^2H^5)^3PO + HCl.$$

(Hofmann, Proc. Roy. Soc. xi. 290.)

**Bromethyl-trimethylphosphonium.** The *bromide*, $(C^2H^4Br)(CH^3)^3PBr$, is formed by digesting a solution of trimethylphosphine in absolute alcohol with a very large excess of ethylenic bromide at 50°—60° for several hours, and separates on cooling in well-defined crystals, which by a few recrystallisations from absolute alcohol, may be obtained perfectly free from adhering diphosphonium-salt. The crystals are trimetric prisms exhibiting the faces $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $oP$, $\infty P$, $2\breve{P}2$. Ratio of axes $a : b : c = 0{\cdot}5681 : 1 : 0{\cdot}4071$ (Phil. Trans. 1860, p. 590).

The *chloroplatinate*, $2(C^2H^4Br)(CH^3)^3PCl.PtCl^4$, crystallises in fine orange-yellow needles.

**Oxethyl-trimethylphosphonium,** $(C^2H^5O)(CH^3)^3P$.—The *hydrate* produced by the action of silver-hydrate on the bromide of bromethyl-trimethylphosphonium forms with hydrochloric acid a very soluble chloride, which yields with tetrachloride of platinum an easily soluble chloroplatinate, $2(C^2H^5O)(CH^3)^3PCl.PtCl^4$, crystallising in octahedrons. (Hofmann.)

## II. DIPHOSPHONIUMS.

**Ethylene-hexethyl-diphosphonium.** $C^{14}H^{34}P^2 = (C^2H^4)''(C^2H^5)^6P^2$.—The *bromide* of this diatomic base, $(C^2H^4)''(C^2H^5)^6P^2Br^2$, is produced by the action of bromide of ethylene on triethylphosphine:

$$C^2H^4Br^2 + 2(C^2H^5)^3P = (C^2H^4)''(C^2H^5)^6P^2Br^2.$$

If the substances are mixed in the exact proportions indicated by this equation (1 vol. bromide of ethylene to 3 vol. triethylphosphine) the bromide of the diphosphonium is obtained nearly pure; but if the bromide of ethylene is in excess of this proportion, the product will likewise contain the bromide of bromethyl-triethylphosphonium (p. 618). As this monatomic bromide is difficult to remove, it is better to prepare the diatomic bromide by saturating the corresponding hydrate with hydrobromic acid. The dibromide is also easily prepared by the action of triethylphosphine on the bromide of bromethyl-triethylphosphonium, its formation taking place in a few minutes in an alcoholic solution heated to 100°.

The dibromide forms white needles, permanent in the air, very soluble in water and in alcohol, insoluble in ether.

On adding bromine-water to the aqueous solution, beautiful yellow, but very unstable needles are formed, probably consisting of a polybromide.

*Bromargentate*, $(C^2H^4)''(C^2H^5)^6P^2Br^2.AgBr$.—When the boiling concentrated alcoholic solution of the diphosphonium-bromide is mixed with as much silver-oxide as it is capable of dissolving, the hot filtrate deposits on cooling, white crystals of the bromargentate which are somewhat difficult to recrystallise from boiling alcohol. The double salt is immediately resolved by water into bromide of silver and the bromide of the diphosphonium.

The bromide decomposed with hydrate of silver yields the corresponding hydrate, which when treated with acids yields the several salts of ethylene-hexethyl-diphosphonium.

***Carbonate.***—Slightly deliquescent, reddens litmus.

***Chloride***, $(C^2H^4)''(C^2H^5)^6P^2Cl^2$.—Produced by saturating the hydrate with hydrochloric acid, or by treating the bromide or iodide with chloride of silver; also when triethylphosphine is mixed with dichloride of ethylene, or heated for some time to 120° with chlorinated ethylic chloride. It forms a broadly-laminar, pearly, very deliquescent crystalline mass, very soluble in water and in alcohol, insoluble in ether. It is precipitated unaltered from its aqueous solution by potash.

*Chloroaurate*, $(C^2H^4)''(C^2H^5)^6P^2Cl^2.2AuCl^3$.—Golden-yellow needles, sparingly soluble in cold water, easily in boiling alcohol.

*Chloropalladite.*—A dilute solution of the diphosphonium-chloride is not precipitated by chloride of palladium; but on adding alcohol, a chocolate-coloured crystalline pulp is formed, consisting of small interlaced needles, the concentrated aqueous solution of which deposits reddish-yellow prisms on slow cooling, and a yellowish-red crystalline powder when quickly cooled.

*Chloromercurate*, $2[(C^2H^4)''(C^2H^5)^6P^2Cl^2].3Hg''Cl^2$.—Thin white laminæ or needles, slightly soluble in water and in alcohol.

*Chloroplatinate*, $(C^2H^4)''(C^2H^5)^6P^2Cl^2.PtCl^4$.—Tetrachloride of platinum produces in the most dilute solutions of the diphosphonium-chloride a pale yellow precipitate, which crystallises from boiling hydrochloric acid in small well developed monoclinic prisms, having an orange-yellow colour and vitreous lustre. Inclination of axes, *b*, *c*, = 82° 36′. Observed faces $\infty P\infty$, $[\infty P\infty]$, $oP$. Cleavage perfect parallel to all three. The salt is nearly insoluble in water, whether cold or boiling.

The *chlorostannite* forms large prisms, probably containing $(C^2H^4)''(C^2H^5)^6P^2Cl^2.2Sn''Cl^2$.

***Chromate.***—Stellate groups of extremely soluble needles, obtained by saturating the hydrate with chromic acid.

***Cyanide.***—This salt is not obtained by saturating the hydrate with hydrocyanic acid; but when the iodide is digested with cyanide of silver, a double salt passes into solution, which crystallises in fine needles, but is very easily decomposible.

***Fluoride.***—The solution of the hydrate saturated with hydrofluoric acid dries up over oil of vitriol to a colourless transparent syrup, soluble in alcohol, insoluble in ether.—The *silico-fluoride* is uncrystallisable.

***Hydrate***, $\left.\begin{matrix}[(C^2H^4)(C^2H^5)^6P^2]'' \\ H^2\end{matrix}\right\}O^2$.—Prepared by adding oxide of silver to an alcoholic solution of the bromide, or better of the iodide, which is more easily obtained pure (*vid. inf.*). The silver-oxide then dissolves, and the solution soon deposits a compound of the bromide or iodide of the diphosphonium with bromide or iodide of silver; but on adding more silver-oxide and a little water, this double salt is decomposed, and a highly caustic, nearly inodorous, but very bitter liquid is obtained, which when filtered and evaporated in the air, takes up carbonic acid and leaves a crystalline mixture of hydrate and carbonate, but dries up in vacuo over oil of vitriol to a very deliquescent, perfectly uncrystalline syrup, from which potash separates the hydrate of ethylene-hexethyl-diphosphonium in oily drops.

The solution of the hydrate is not altered by heating to 150°, but begins to decompose at 160°, and is completely decomposed at 250°, the ultimate products of the distillation being triethylphosphine, oxide of triethylphosphine, ethylene-gas and water:

$$(C^2H^4)''(C^2H^5)^6P^2H^2O^2 \;=\; (C^2H^5)^3P + (C^2H^5)^3PO + C^2H^4 + H^2O.$$

As intermediate products are obtained the hydrate of tetrethylphosphonium and probably also hydrate of oxethyl-triethylphosphonium.

The solution of the hydrate reacts with metallic salts in the same manner as hydrate of potassium, excepting that the precipitate of zinc-hydrate formed by it in *zinc-solutions* is insoluble in excess of the precipitant, and that the precipitates formed in acid solutions of *antimonious chloride* and *stannous chloride* are double salts crystallising in interlaced needles. The hydrate separates *ammonia, aniline, triethylphosphine* and many other amines and phosphines from their salts. It has no action upon *phosphorus*, but dissolves *sulphur*, forming a yellow liquid which when treated with acids, gives off sulphydric acid and yields a precipitate of sulphur, and precipitates lead from its salts as sulphide. It dissolves *iodine* with facility; and on mixing the colourless solution which contains the iodide and iodate of the diphosphonium, with strong hydrochloric acid, it solidifies, after transient dark coloration and turbidity, to a lemon-yellow crystalline mass which crystallises from alcohol in fine needles, and is probably a compound of the diphosphonium-iodide with chloride of iodine.

*Iodate.*—Very deliquescent syrup which solidifies very slowly to a crystalline mass.

*Iodide,* $(C^2H^4)''(C^2H^5)^6P^2I^2$.—When the mother-liquors obtained in the preparation of bromide of bromethyl-triethylphosphonium (p. 618), are treated with silver-oxide, and the filtrate is saturated with hydriodic acid, a solution is formed containing iodide of ethylene-hexethyl-diphosphonium, and iodide of oxethyl-triethylphosphonium, which are easily separated by crystallisation, as the latter is very soluble in cold water and alcohol, and remains wholly in the mother-liquors after the second recrystallisation.

The diphosphonium-iodide crystallises in white trimetric needles, elongated in the direction of the brachydiagonal, and consisting of combinations of the faces $\infty P$, $\breve{P}\infty$, with others which cannot be exactly determined on account of curvature. Angle $\infty P : \infty P = 59° 24'$; $\breve{P}\infty : \breve{P}\infty$ over the principal axis $= 89° 42'$. The crystals cleave perfectly parallel to $\infty P$ and $\breve{P}\infty$, and have a vitreous lustre on the faces $\infty P$, nacreous on $\breve{P}\infty$. The smaller crystals are transparent, the larger ones milky and hollow. The salt melts without decomposition at 231°, and decomposes at higher temperatures, with formation of a brown substance not further examined. Heated with caustic baryta it gives off triethylphosphine. 100 pts. water dissolve 458·3 pts. of it at 100°, and only 3·08 pts. at 12°; it is but slightly soluble in alcohol, and insoluble in ether. Potash precipitates it in the crystalline state, even from dilute solutions. It forms double compounds with various metallic salts.

*Iodozincate,* $(C^2H^4)''(C^2H^5)^3P^2I^2.Zn''I^2$.—Formed on mixing the aqueous solutions of the component salts, as a crystalline precipitate which separates from hot water in long needles.

*Nitrate.*—Laminæ permanent in the air, very soluble in water, less soluble in alcohol, and precipitated from alcoholic solution by ether as an oil. Forms with mercuric chloride a precipitate which crystallises in needles.

*Oxalate.*—Slightly crystalline.

*Perchlorate,* $(C^2H^4)''(C^2H^5)^6P^2.Cl^2O^8$.—Beautiful needles often an inch long; may be dried at 100° without decomposition, but detonates with a higher temperature.

*Phosphate.*—Obtained by boiling the iodide with excess of silver-phosphate. Slightly crystalline.

*Picrate.*—Separates on adding picric acid to a moderately strong solution of the hydrate, as a yellow crystalline precipitate which separates from the boiling alkaline solution in long needles.

*Sulphate.*—Radio-crystalline, very deliquescent.

*Sulphocyanate.*—The aqueous solution produced by boiling the iodide with recently precipitated sulphocyanate of silver, dries up over the water-bath to a crystalline mass, soluble in water and in alcohol, but precipitated from the alcoholic solution by ether.

*Sulphydrate.*—The solution of the hydrate saturated with sulphydric acid leaves a gummy mass when evaporated in vacuo over oil of vitriol. If evaporated over the water-bath with access of air, it leaves the crystalline sulphate.

*Tartrate.*—Extremely soluble; difficult to crystallise.

### *Appendix to the Compounds of Ethylene-hexethyl-diphosphonium.*

**Paradiphosphonium compounds.**—When the aqueous solution of hydrate of ethylene-diethyl-diphosphonium is evaporated in a retort filled with hydrogen, it begins to decompose as above mentioned at 160°; and if the dry distillation be interrupted as soon as the heat has risen to about 190°, the alkaline residue then remaining yields with hydrochloric acid and a small quantity of platinic chloride, no longer the pale yellow crystalline precipitate of chloroplatinate of ethylene-hexethyl-diphosphonium, perfectly insoluble in water and in dilute hydrochloric acid, but an amorphous dirty yellow salt, easily soluble in hydrochloric acid. If the dingy precipitate produced by the first drops of the platinum-solution be filtered off, and the filtrate treated with a

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further quantity of the platinum-solution, the amorphous platinum double salt is obtained quite pure and of a light yellow colour. The same double salt is produced by similar treatment of the hydrate of oxethyl-triethylphosphonium; also by adding hydrochloric acid and platinic chloride to the mixture of hitherto unexamined products formed by prolonged heating of monobrominated ethylene (bromide of vinyl, $C^2H^3Br$) with triethylphosphine to 160°—180°. It has the same percentage composition as the chloroplatinate of ethylene-hexethyl-diphosphonium. If the amorphous pale yellow precipitate suspended in water be decomposed by sulphydric acid, and the filtrate, freed from the excess of that gas, be treated with silver-oxide, the resulting solution of paraethylene-hexethyl-diphosphonium hydrate yields, when saturated with hydriodic acid and evaporated, a gummy mass which slowly becomes crystalline, and after repeated crystallisation is identical with the iodide of ethylene-hexethyl-diphosphonium. Hence it appears that the paradiphosphonium salts are gradually reconverted into ordinary diphosphonium-salts. (Hofmann, Phil. Trans. 1860, p. 533.)

**Ethylene-triethyl-trimethyl-diphosphonium.** The *bromide* of this radicle, $(C^2H^4)''(C^2H^5)^3(CH^3)^3P^2Br^2$, is produced, with violent action, by treating the bromide of bromethyl-triethylphosphonium with trimethylphosphine. It is more soluble than the bromide of the hexethylated base, which it resembles in other respects. When digested with moist silver-oxide it yields an extremely caustic hydrate, which forms with hydrochloric acid and platinic chloride a pale yellow scaly *chloroplatinate* containing $(C^2H^4)''(C^2H^5)^3(CH^3)^3P^2Cl^2.PtCl^4$.

**Ethylene-hexmethyl-diphosphonium.** The *bromide*, $(C^2H^4)''(CH^3)^6P^2Br^2$, is produced by treating bromide of ethylene at 100° with excess of trimethylphosphine. It is extremely deliquescent, but may be obtained with some difficulty in well-developed monoclinic crystals having the axes $a : b : c = 1{\cdot}05445 : 1 : 1{\cdot}1255$, the angle of the axes $b, c = 37° 49'$, and exhibiting the faces oP, ∞P, [P∞]. Angle ∞P : ∞P (orthod.) = 83° 13'; oP : ∞P = 121° 38'; +P∞ : ∞P = 99° 8'.

The *chloroplatinate*, $(C^2H^4)''(CH^3)^6P^2Cl^2.PtCl^4$, obtained in the usual way, is a yellow, apparently amorphous precipitate which crystallises from boiling hydrochloric acid in golden-yellow laminæ.

The *iodide*, $(C^2H^4)''(CH^3)^6P^2I^2$, obtained by saturating the hydrate with hydriodic acid, forms beautiful sparingly soluble needles.

## III. PHOSPHAMMONIUMS.

**Ethylene-triethylphosphammonium.** $C^8H^{22}NP = \left.\begin{matrix}(C^2H^4)''\\(C^2H^5)^3\\H^3\end{matrix}\right\}\begin{matrix}N\\P\end{matrix}$.—The *bromide* of this diatomic base is obtained by digesting an alcoholic solution of bromide of bromethyl-triethylphosphonium with ammonia for half an hour in a sealed tube at 100°. On leaving the alcohol to evaporate, the phosphammonium-bromide remains slightly contaminated with bromide of ammonium:

$$(C^2H^4Br)(C^2H^5)^3PBr \quad + \quad NH^3 \quad = \quad (C^2H^4)''(C^2H^5)^3H^3PN.Br^2.$$

The pure salt is best obtained by saturating the hydrate with hydrobromic acid. It crystallises pretty well, but is very deliquescent.

The *chloride* and *iodide* resemble the bromide.—The *perchlorate* is sparingly soluble and crystallises readily.

The *chloroaurate*, $(C^2H^4)''(C^2H^5)^3H^3PNCl^2.2AuCl^3$, is a golden-yellow precipitate consisting of slender needles, sparingly soluble in water.

The *chloroplatinate*, $(C^2H^4)''(C^2H^5)^3H^3NPCl^2.PtCl^4$, is obtained as a pale yellow, slightly crystalline precipitate, which dissolves sparingly in boiling water, and crystallises from hot concentrated hydrochloric acid in well-developed trimetric prisms, exhibiting the faces $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $\infty P$, $\breve{P}\infty$. Angle $\infty P : \infty P = 119° 40'$; $\breve{P}\infty : \infty\breve{P}\infty = 160° 38'$. Hardness somewhat greater than that of gypsum.

The *hydrate*, $\left.\begin{matrix}(C^2H^4)''(C^2H^5)^3H^3NP\\H^2\end{matrix}\right\}O^2$, obtained by treating the bromide with silver-oxide, may be concentrated without change at the heat of the water-bath, and finally separated by potash in oily drops. When more strongly heated it gives off ammonia and leaves hydrate of vinyl-triethylphosphammonium:

$$(C^2H^4)''(C^2H^5)^3H^3NP.H^2O^2 \quad = \quad (C^2H^3)(C^2H^5)^3PHO \quad + \quad NH^3 \quad + \quad H^2O.$$

**Ethylene-tetrethylphosphammonium.** $(C^2H^4)''(C^2H^5)^4H^2NP$.—The *bromide* is obtained by the combination of ethylamine with bromide of bromethyl-triethylphosphonium (p. 608).—The *hydrate* may be separated from its solution in oily drops by concentration over the water-bath. It yields salts by saturation with acids.

The *iodide*, $(C^2H^4)''(C^2H^5)^4H^2NP.I^2$, forms white needles, easily soluble in water and in aqueous alcohol, sparingly soluble in absolute alcohol, insoluble in ether. Potash precipitates it from its aqueous solution without decomposition, as an oil which gradually solidifies.

The *chloroaurate*, $(C^2H^4)''(C^2H^5)^4H^2NPCl^2.2AuCl^3$, forms golden-yellow, sparingly soluble needles.—The *chloroplatinate*, $(C^2H^4)''(C^2H^5)^4H^2NPCl^2.PtCl^4$, crystallises in orange-yellow, trigonal-tabular or sphenöidal monoclinic combinations, $\infty P\infty$ . oP. $\infty P$ . $[\infty P\infty]$, usually hemimorphously developed, sometimes on one, sometimes on the other side of the orthodiagonal. Angle $\infty P : oP = 93° 8'$; $\infty P : \infty P$ in the orthodiagonal principal section $= 89° 50'$; $[P\infty] : [P\infty]$ in the clinodiagonal principal section $= 90° 29'$; $oP : \infty P\infty = 86° 52'$.

**Ethylene-pentethyl-phosphammonium.** $(C^2H^4)''(C^2H^5)^5HNP$.—The *bromide* is formed by the action of diethylamine on bromide of bromethyl-triethylphosphonium. —The *chloroplatinate*, $(C^2H^4)''(C^2H^5)^5HNPCl^2.PtCl^4$, crystallises in rectangular plates.

**Ethylene-triethyl-methylphosphammonium.** The *bromide* is formed by digesting methylamine with bromide of bromethyl-triethylphosphonium.—The *platinum-salt*, $(C^2H^4)''(C^2H^5)^3(CH^3)H^2NPCl^2.PtCl^4$, crystallises in long needles, very sparingly soluble.

**Ethylene-triethyl-trimethylphosphammonium.** The *bromide* is produced by the union of trimethylamine with bromide of bromethyl-triethylphosphonium.—The *platinum-salt*, $(C^2H^4)(C^2H^5)^3(CH^3)^3NPCl^2.PtCl^4$, crystallises in beautiful needles.

## IV. PHOSPHARSONIUMS.

The only salts of this group yet discovered are those of—

**Ethylene-hexethylphospharsonium.** The *bromide*, $(C^2H^4)''(C^2H^5)^6PAsBr^2$, is produced by digesting bromide of bromethyl-triethylphosphonium with triethylarsine in a sealed tube. When digested in the cold with moist oxide of silver, it is converted into the *hydrate*, $(C^2H^4)''(C^2H^5)^6PAs.H^2O^2$, the solution of which is resolved by boiling into hydrate of oxethyl-triethylphosphonium and triethylarsine:

$$(C^2H^4)''(C^2H^5)^6PAsH^2O^2 \quad = \quad (C^2H^5O)(C^2H^5)^3PHO \quad + \quad (C^2H^5)^3As.$$

The hydrate saturated with hydrobromic or hydriodic acid yields the bromide or iodide in fine needles.

The *chloroplatinate*, $(C^2H^4)''(C^2H^5)^6PAsCl^2.PtCl^4$, is obtained by adding platinic chloride to the aqueous solution of the phospharsonium-chloride, as a pale yellow precipitate which is nearly insoluble in water, and crystallises from boiling hydrochloric acid in orange-red triclinic prisms, $\infty\breve{P}\infty$ . $\infty\breve{P}\infty$ . oP . $,\breve{P}\infty$ . $2\breve{P},\infty$ . $P'$. Angle $\infty\breve{P}\infty : \infty\breve{P}\infty = 98° 8'$; $\infty\breve{P}\infty : oP = 91° 46'$; $P' : \infty\breve{P}\infty = 115° 56'$; $2\breve{P}\infty : \infty\breve{P}\infty = 145° 35'$; $\breve{P}'\infty : \infty\breve{P}\infty = 126° 57'$. The crystals cleave parallel to $\infty\breve{P}\infty$ and oP.

## V. TRIPHOSPHONIUM-COMPOUNDS.

When triethylphosphine is gradually mixed with crystals of *iodoform* as long as any rise of temperature is thereby produced, a light yellow viscid mass is formed, the solution of which in boiling alcohol deposits crystals of iodide of formyl-ennethyltriphosphonium, $(CH)'''(C^2H^5)^9P^3I^3$. This salt dissolves easily in water and sparingly in alcohol, but is insoluble in ether. *Iodide of zinc* added to the aqueous solution throws down a white double salt containing $2(C^2H)'''(C^2H^5)^9P^3I^3.3Zn''I^2$. *Tetrachloride of platinum* forms a light yellow precipitate of a platinum-salt, $2(CH)'''(C^2H^5)^9P^3Cl^3$. $3PtCl^4$, which crystallises from boiling alcohol in rectangular laminæ. The iodide treated with *oxide of silver* does not yield the corresponding hydrate, but undergoes decomposition, forming hydrate of methyl-triethylphosphonium and oxide of triethylphosphine:

$$(CH)'''(C^2H^5)^9P^3I^3 \ + \ 3AgHO \ = \ 3AgI \ + \ (CH^3)(C^2H^5)^3PHO \ + \ 2(C^2H^5)^3PO.$$

Triethylphosphine treated with chloroform or with tetrachloride of carbon yields the chloride of formyl-ennethyl-triphosphonium. (Hofmann, Proc. Roy. Soc. x. 189; xi. 290.)

**PHOTOCHEMISTRY.** See LIGHT, CHEMICAL ACTION OF (iii. 678).

**PHOTOGEN.** A term applied to the light hydrocarbon oils obtained by distilling coal, shale, peat, &c., at low temperatures, and used for burning in lamps. (See PARAFFIN, pp. 344–349.)

**PHOTOGRAPHY.** The history of the art of producing sun-pictures, and a sketch of the several methods, have already been given in the article on the Chemical Action of Light (iii. 692). The present article contains a more detailed account of some of the processes now in use.

### A. *Processes in which Silver-salts are used.*

### I. *Wet Collodion Process.*

1. The photographic collodion is prepared by dissolving 5 grms. of gun-cotton or pyroxylin, carefully washed and neutral to test-paper, in a mixture of 200 cub. cent. of alcohol of 40 per cent., and 300° cub. cent. ether of 62 per cent.; and to this solution is added a mixture of 45 grms. of cadmium-iodide with a little ammonium-iodide, and 1·25 grm. cadmium-bromide with a trace of ammonium-bromide, all finely pulverised.

2. To prepare the sensitive surface, a plate of glass free from flaws, thoroughly cleansed by washing with water, nitric acid, alcohol, &c., and quite free from dust, is covered with the prepared collodion, and plunged wet *at one dip* in a solution of silver-nitrate containing 8 pts. of the salt in 100 pts. of water. The coagulated collodion then imprisons within its pores the iodide and bromide of silver resulting from the chemical reaction, and thus forms a continuous sensitive film. The plate is then exposed to the action of light in the camera for an interval varying from 30 seconds to 5 minutes according to the intensity of the light.

3. *Developement of the Picture.*—The exposure of the plate in the manner just mentioned does not produce any visible image; but the iodide and bromide of silver in the film have undergone a certain change, their atoms having apparently acquired a certain degree of mobility, in consequence of which, when submitted to the action of reducing agents, such as ferrous sulphate or pyrogallic acid, they suffer decomposition, the silver being reduced to the metallic state and forming an opaque metallic film on those parts of the surface which have been exposed to the light. To effect this reduction, the sensitive plate, immediately after its removal from the camera, is washed with one of the two following solutions:

| | |
|---|---|
| Saturated solution of ferrous sulphate . . . . | 100 c. c. |
| Filtered water . . . . . . . . . . | 700 „ |
| Glacial acetic acid . . . . . . . . . | 20 „ |
| Alcohol of 36° . . . . . . . . . . | 20 „ |

Or:

| | |
|---|---|
| Water . . . . . . . . . . . | 250 „ |
| Acetic acid . . . . . . . . . . | 20 „ |
| Pyrogallic acid . . . . . . . . . . | 1 grm. |

4. *Strengthening* (*Renforçage*). This necessary but very delicate operation consists in washing the plate with a solution of 2 grms. nitrate of silver, 100 c. c. distilled water and 5 c. c. alcohol,—then with one of the developing solutions above mentioned, then again with the strengthening liquid, and so on, till the picture has acquired the proper degree of intensity. Or instead of subjecting the plate to these alternate washings, it may be immersed in a mixture of the developing and strengthening solutions made just before it is wanted for use. The plate is then carefully washed with pure water.

5. *Fixing*—To remove the undecomposed portions of iodide and bromide of silver, and thus protect the picture from the further action of light, the plate is immersed either in a solution of *cyanide of potassium* containing 2 per cent. of the salt, or in a solution of *hyposulphite of sodium* containing 25 per cent., then washed carefully with a large quantity of water.

The last operation consists in *varnishing* the picture, the plate having been previously heated so that the varnish may spread over it uniformly.

The picture obtained by this process is, as already observed (iii. 693), a negative picture, the parts most strongly acted upon—which of course correspond with the brightest parts of the object—being the darkest. To obtain positive pictures, a sheet of white paper of good quality is covered on one surface with a layer of albumin mixed with a convenient quantity of sal-ammoniac. It is then rendered sensitive by laying it for a while on a solution of nitrate of silver of the strength of 15 per cent., taking care to avoid the presence of air-bubbles between the paper and the surface of the liquid. The albumin thus becomes impregnated with chloride of silver. The paper thus prepared is placed when dry behind the negative picture, and exposed to light, whereby the chloride of silver is reduced on those parts which are behind the transparent parts of the negative, while those portions of the surface which are behind the opaque parts of the negative remain unaltered.

The silver thus reduced has, however, an unpleasant red colour, and to obtain a darker and more agreeable tint, the picture is steeped in a gold-bath composed of 1000 grms. distilled water, 30 grms. neutral acetate of sodium, and 1 grm. trichloride of gold mixed with chloride of potassium. As soon as the desired tint has been obtained, an effect which is rapidly produced at the temperature of 25° C., the picture is to be fixed by immersing it in a bath composed of 600 grms. distilled water and 100 grms. hyposulphite of sodium, then washed several times during 12 hours with distilled water. These operations of toning and fixing must be performed in a room from which daylight is excluded.

To ensure success in the process above described, attention must be paid to certain precautions: 1. The silver-bath used for obtaining the negative must be slightly acid. If it is neutral or basic, the image will be cloudy and deficient in strength in the darker points; if it is too acid, the production of the picture takes place slowly. If it is either supersaturated or insufficiently charged with iodide of silver, especially if the film of collodion is not very thick, the negative obtained will be full of holes.—2. The glass must be free from defects and thoroughly freed from dust, otherwise partial reduction of the silver takes place before the plate is exposed to the action of the developing solution.

The great objection to photographs on paper is their alterability. In connection with this the following fact is interesting. The hyposulphite of sodium used for removing the excess of silver-chloride forms sodio-argentic hyposulphites, one of which being but very slightly soluble, remains in the paper and gradually decomposes, ultimately destroying the picture; whereas the other, which is formed when the hyposulphite of sodium is in large excess, is very soluble, so that when the latter condition is fulfilled, the subsequent washing removes nearly all if not the whole of the alterable substance remaining on the paper. Photographs fixed within the last few years with due attention to this circumstance have remained unaltered up to the present time.

The author of this article proposed two years ago to remove the hyposulphites by the use of chlorine-water, free from hydrochloric acid, and added in proportion to the quantity of hyposulphite which might remain in the picture: an excess would give rise to the chlorination of the gold and silver in the picture. The hyposulphite might also be converted into sulphate by means of a solution of oxygenated water, recently prepared with peroxide of barium and carbonic acid, and freed from excess of the latter by means of baryta-water.

*Direct Positives on Glass.*—The picture obtained on a sensitive collodion plate by very short exposure in the camera, and very slight developement, may serve as a positive when placed upon a black ground. Under these conditions, the very small quantity of silver reduced on the lights of the picture conceals the black ground, and appears white, whilst in the parts corresponding to the shadows of the object no silver is reduced, and the black ground shows through. The collodion for these pictures is prepared with 300 c. c. water, 125 c. c. alcohol, and 3 grms. pyroxylin; and to this is added a mixture of 175 c. c. alcohol, 7 grms. iodide of ammonium, and 0·7 grm. nitrate of silver. The plate is rendered sensitive by immersion in a bath of silver-nitrate containing 5 per cent. of the salt acidulated with a few drops of nitric acid; and after a very short exposure in the camera, the picture is developed with a mixture of 100 c. c. saturated solution of ferrous sulphate, 600 grms. water, 20 grms. acetic acid, 20 grms. alcohol, and 5 grms. sulphuric acid, and fixed with cyanide of potassium. Lastly the back of the glass plate is covered with a mixture of oil of turpentine, Mecca balsam, and lamp-black.

### II. *Dry Collodion Process.*

This process, which differs from the preceding only in the mode of obtaining the negative, has the advantage of enabling the operator to prepare beforehand a large supply of sensitive plates, and thus to take a considerable number of pictures on the same day, a convenience which is especially valuable in landscape photography.

The best mode of proceeding is to cover the collodion plate—rendered sensitive as usual by immersion in a slightly acid silver-bath, then washed several times in distilled water—with a solution of tannin freed from resinous matter and having a strength of 3 per cent. The plates thus prepared are as sensitive after the lapse of several months as immediately after preparation. The picture is developed with pyrogallic acid.

Other modifications of the dry collodion process are Tamponot's process with albuminised collodion, and those in which the dry collodion film is covered with sugar, honey, metagelatin, &c.; but none of these are equal to the tannin process just mentioned, which is due to Major Russell.

### III. *Albumin Process on Glass.*

This process, due to Niepce de St. Victor, includes the taking of both negatives and positives on albuminised plates. A layer of albumin impregnated with iodide of potassium is rendered sensitive in a bath composed of 100 grms. water, 10 grms. nitrate of silver, and 10 grms. acetic acid. The picture is developed with gallic acid,

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fixed with hyposulphite of sodium, and brought to an agreeable tint by means of chloride of mercury or chloride of gold.

### B. *Photographic Processes without Silver-salts.*

1. *Photography with Carbon, Ferrous salts or Uranium-salts.*—Of these three methods, the first is that which yields the best results. It depends on the action of light on the salts of chromic acid and on gelatin or a similar substance.

A sheet of paper impregnated with these matters is placed behind a negative and exposed to light, whereby the substances are rendered insoluble in the parts corresponding to the transparent portion of the negative, and therefore to the dark parts of the original object. The parts thus altered are alone capable of retaining porphyrised black, or coloured powders, or lithographic ink, subsequently applied to the surface of the paper.

The processes depending on the use of ferrous and uranic salts present no particular interest.

2. The processes of photolithography, photozincography, that called heliography discovered by Niepce in 1827, and photogalvanography are described in the article LIGHT (iii. 694). The last-mentioned process, depending upon the property possessed by certain substances, chromatised gelatin for example, of losing, by insolation, the power of swelling up in water, or when exposed to the action of steam, was invented by M. Poitevin, and has lately been much improved by a very skilful operator of Paris, M. Villeneuve, who has advantageously modified the manipulations, and replaced the gelatin by another substance, the composition of which, however, he keeps secret. The impressions obtained from the plates formed by his process are extremely delicate.

For further details, see Pelouze et Frémy, *Traité de Chimie*, 3me ed. iii. 1429-1486.

A method of measuring the relative sensitiveness of different photographic papers is described by A. McDongall in the Journal of the Chemical Society, vol. xviii. p. 183.

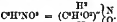
A. H.

**PHOTOSANTONIN.** $C^{11}H^{14}O^{3}$. (F. Sentini, Bull. Soc. Chim. 1864, ii. 21; 1865, i. 271.)—A neutral substance, produced, together with formic acid, by the action of light on santonin. The change takes place slowly under the influence of diffused daylight, more quickly on exposing santonin, either dry or in contact with water, to the action of the direct solar rays; but the transformation is not complete even after three months' exposure. A better mode of effecting it is to expose an alcoholic solution of santonin, freed from air by passing carbonic anhydride through it and then sealing it in a tube, to sunshine for about a month. The liquid then acquires a yellow colour, and when it is subsequently mixed with about fifteen times its volume of water, the photosantonin separates in oily drops, which, in the course of a day or two, crystallise in white laminæ: it may be purified by two or three crystallisations from alcohol. The last portions which separate have a yellow colour, arising from a resinous substance; this may be dissolved out by leaving the photosantonin for two days in contact with cold potash-ley, which also favours the crystallisation of the photosantonin.

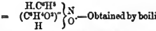
Photosantonin is colourless and transparent, destitute of odour, but has a slight bitter taste. It crystallises in square plates, which have no action on polarised light, a character by which this substance is easily distinguished from santonin. It melts between 64° and 65°, begins to give off vapour at 180°, and boils at 305°. It is insoluble in cold water, but dissolves in boiling *water* sufficiently to impart a distinctly bitter taste; *alcohol* and *ether* dissolve it in large quantity, forming very bitter solutions.

Photosantonin, exposed to the *air* for nine or ten months at 100°, diminishes slightly in weight, and is partly converted into a yellow resin soluble in potash. In contact with strong *nitric acid*, it liquefies, forming drops which float on the acid. Strong *sulphuric acid* colours it orange-yellow, and then decomposes it.

**PHTHALAMIC ACID.** $C^{8}H^{7}NO^{3} = \left.\begin{matrix}H^{2}\\(C^{8}H^{4}O^{2})''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Marignac, Ann. Ch. Pharm. xlii. 219.—Lanront, Rev. scient. xiii. 601.)—Produced by the action of aqueous ammonia on phthalic anhydride. Crystallises in a mass of fine flexible needles, forming an acid solution with water. It gives off water between 100° and 120°, and is converted into phthalimide, $C^{8}H^{5}NO^{2}$, which sublimes at a higher temperature. The aqueous solution, after boiling for some time, yields phthalate of ammonium on evaporation.



*Phthalamate of silver*, $C^{8}H^{6}AgNO^{3}$, is a white precipitate, composed of crystalline scales if formed with boiling solutions. It is quite insoluble in water; melts when heated, and decomposes without explosion.

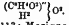


$$\left.\begin{matrix}H.C^6H^5\\(C^8H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$$

***Phenyl-phthalamic acid***, $C^{14}H^{11}NO^3 = \left.\begin{matrix}H.C^6H^5\\(C^8H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—Obtained by boiling phenyl-phthalimide, $C^{14}H^9NO^2$, with aqueous ammonia containing a little alcohol. The liquid, if neutralised with nitric acid while still hot, yields, on cooling, a fine, irregularly laminated crystalline mass of phenyl-phthalamic acid. The acid is very slightly soluble in cold water, but dissolves easily in alcohol. When fused with potash at a gentle heat, it gives off aniline. When saturated with ammonia, it gives a white precipitate with nitrate of silver. (Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 188.)

**PHTHALAMINE.** $C^8H^9NO^2$.—A base produced, together with naphthylamine, by the action of ferrous acetate on nitronaphthalene. The two bases may be separated by treating the crude product with sulphuric acid, the sulphate of phthalamine, $2C^8H^9NO^2.H^2SO^4.2H^2O$, being more soluble than the naphthylamine salt.

Phthalamine is precipitated from the solution of its sulphate by ammonia in oily drops, which are heavier than water and taste like naphthylamine: its salts do not redden so easily on exposure to the air as those of the latter. The base heated to 100° with iodide of ethyl, solidifies in a few minutes to a laminar mass of iodide of ethyl-phthalamine, $C^8H^8(C^2H^5)NO^2I$(?), which when treated with ammonia yields an oily base, altering on exposure to the air, and volatilising at about 300°. (Schützenberger and Willm, J. pr. Chem. lxxiv. 75.)



$$\left.\begin{matrix}(C^8H^4O^2)''\\H^2\end{matrix}\right\}O^2$$

**PHTHALIC ACID.** $C^8H^6O^4 = \left.\begin{matrix}(C^8H^4O^2)''\\H^2\end{matrix}\right\}O^2$. *Alizaric acid, Naphthalic acid.* (Laurent, Ann. Ch. Phys. [2] lxi. 113; Marignac, Ann. Ch. Pharm. xlii. 215; Schunck, *ibid.* lxvi. 197; Wolff and Strecker, *ibid.* lxxv. 12, 25; Hugo Müller, *Epistolary communication.*)—An acid produced by the action of nitric acid on naphthalene, dichloride of naphthalene, alizarin, and purpurin:

$$\underset{\text{Naph-thalene.}}{C^{10}H^8} + O^8 = \underset{\text{Phthalic acid.}}{C^8H^6O^4} + \underset{\text{Oxalic acid.}}{C^2H^2O^4}.$$

$$\underset{\text{Alizarin.}}{C^{10}H^6O^3} + H^2O + O^4 = C^8H^6O^4 + C^2H^2O^4.$$

$$\underset{\text{Purpurin.}}{2C^9H^6O^3} + H^2O + O^5 = 2C^8H^6O^4 + C^2H^2O^4.$$

It is usually prepared by treating dichloride of naphthalene with boiling nitric acid. The dichloride dissolves slowly with evolution of nitrous vapours, and the solution, when left to itself, deposits crystals of phthalic acid, which may be purified by recrystallisation from boiling water. The mother-liquor contains oxalic acid. Small quantities of phthalic acid are found in the mother-liquors obtained in preparing the nitro-derivatives of naphthalene.

Phthalic acid may also be prepared by digesting munjistin (a body closely related to alizarin and purpurin, iii. 1061) with moderately strong nitric acid. The resulting solution evaporated over the water-bath leaves a white crystalline mass, consisting of phthalic acid contaminated only with a little oxalic acid. The latter is easily removed by washing the mass with cold water and pressing between bibulous paper, or by neutralising the mixture of the two acids with lime, and then treating it with boiling water, which dissolves the phthalate of calcium. (Stenhouse, Ann. Ch. Pharm. cxxx. 334.)

Phthalic acid crystallises in white nacreous laminæ arranged in rounded groups. It is sparingly soluble in cold *water*, but dissolves easily in *alcohol* and *ether*. By distillation it is converted into phthalic anhydride; this process is recommended by Stenhouse for the purification of the acid. When distilled with excess of lime (or any caustic alkali) it is resolved into benzene and a carbonate (Marignac, Schunck):

$$C^8H^6O^4 + 2Ca''O = C^6H^6 + 2CCa''O^3;$$

but by distillation with a smaller proportion of lime, it is converted into carbonate and benzoate of calcium:

$$2C^8H^6O^4 + 3Ca''O = C^{14}H^{10}Ca''O^4 + 2CCa''O^3 + H^2O,$$

or

$$2C^8H^4Ca''O^4 + Ca''H^2O^2 = C^{14}H^{10}Ca''O^4 + 2CCa''O^3.$$

This latter reaction is used by P. and E. Depouilly (Bull. Soc. Chim. 1864, i. 163) for the industrial preparation of benzoic acid (to be employed in the manufacture of certain aniline colours). The phthalic acid required for the purpose is obtained by treating dichloride of naphthalene with hydrochloric acid and chlorate of potassium.

Phthalates. Phthalic acid is dibasic, forming acid salts, $C^8H^5MO^4$, and neutral salts, $C^8H^4M^2O^4$.

The *acid ammonium-salt*, $C^8H^5(NH^4)O^4$, usually crystallises in prisms terminated by four- or eight-sided pyramids, frequently also in hexagonal plates. The crystals belong to the trimetric system. Observed combination $oP . P . \breve{P}\infty$. Angle $oP : P = 112°$; $P : P = 133° 50'$; $oP : \breve{P}\infty = 127°$; $\breve{P}\infty : \breve{P}\infty = 103° 30'$. Cleavage easy parallel to oP. It is very soluble in water, sparingly soluble in alcohol, and is resolved by heat into water and phthalimide. The *potassium-* and *sodium-salts* crystallise in very soluble scales.

The *barium-salt* crystallises in slightly soluble scales, which may be obtained by pouring a strong solution of the ammonium-salt into chloride of barium. The *calcium-salt*, obtained by dissolving calcic carbonate in the aqueous acid, resembles the barium-salt. Its decomposition by heat has been already described.

The *lead-salt*, $C^8H^4Pb''O^4$, is obtained in white scales on mixing the boiling solutions of acetate of lead and phthalate of ammonium.

The *silver-salt*, $C^8H^4Ag^2O^4$, obtained in like manner by precipitation from boiling solutions, is a white crystalline precipitate which requires prolonged washing, as it obstinately retains nitrate of ammonium. It is moderately soluble in water. It explodes when quickly heated, but if the heat be cautiously applied, the salt blackens, then melts and decomposes.

The *zinc-salt* is obtained by evaporation as a crystalline powder nearly insoluble in cold water.

### *Substitution-derivatives of Phthalic acid.*

Phthalic acid resists in a remarkable degree the action of chlorine, bromine, sulphuric anhydride and nitric acid, and it is only with great difficulty that substitution-compounds can be obtained.

**Bromophthalic acid.** Bromine heated with phthalic acid in a closed tube, does not seem to act upon it, but if water is present and the temperature is raised to about 170°, bromophthalic acid is formed. This acid crystallises readily in foliated crystals which are soluble in water, and sublime when heated, after fusion, without decomposition. The *silver-salt* is a crystalline precipitate somewhat soluble in water.

Bromophthalic acid is remarkably stable, and can be boiled with water without decomposition. The bromine cannot be removed by the action of potash or of silver-salts, in which respect, bromophthalic acid comports itself very differently from the analogous compound bromosuccinic acid. (Hugo Müller.)

**Chlorophthalic acids.** Chlorine in the free state, or in the form of antimonic chloride, has no action on phthalic acid, the only known chlorinated derivatives of this acid being those which are obtained indirectly by the action of nitric acid on the chloronaphthalenes.

*Dichlorophthalic acid*, $C^8H^4Cl^2O^4$, was once obtained (together with another acid, probably di- or tri-chloronapthalic acid) in the preparation of chloroxynaphthalic (chloronaphthalic) acid (p. 14). On saturating the boiling alcoholic solution with potash, the potassium-salt separated in silvery laminæ, having when dried at 100°, the composition $C^8H^2Cl^2K^2O^4$. (Wolff and Strecker, Ann. Ch. Pharm. lxxv. 16.)

*Trichlorophthalic acid*, $C^8H^3Cl^3O^4$.—When hexchloronaphthalene is boiled for several days with nitric acid and the product is mixed with water, a resinous mass separates out, and the solution yields on evaporation, a crystalline magma of trichlorophthalic acid, which after repeated pressure between blotting paper and recrystallisation from boiling water, is obtained in crystalline grains. It is very soluble in water, alcohol and ether. When heated, it is resolved into water and trichlorophthalic anhydride, $C^8HCl^3O^3$. The ammonium-salt forms a white precipitate with salts of silver. (Laurent.)

**Nitrophthalic acid**, $C^8H^5NO^6 = C^8H^5(NO^2)O^4$.—This acid is best prepared by the prolonged action of nitric acid upon naphthalene. It is contained in the mother-liquors from which the nitronaphthalenes (p. 15) have been deposited, and may be separated therefrom by evaporating the liquid to a syrup, dissolving the residue in water, filtering, and again evaporating. The last mother-liquors also contain phthalic acid (Laurent, Marignac).—Nitrophthalic acid is also formed, together with other products, when phthalic acid is treated with pure nitric acid, or with a mixture of nitric and sulphuric acids. (Hugo Müller.)

Nitrophthalic acid crystallises in yellow plates, derived from a monoclinic prism, but ordinarily rendered hexagonal by the truncation of the acute angles of the rhombus. Angle $oP : \infty P = 104°$; $\infty P : \infty P =$ about 125°; $oP : \infty P\infty = 124°$. Most of the crystals are hemitropic. The acid is moderately soluble in boiling water, sparingly soluble in cold water, easily in alcohol and ether. When slightly heated in a tube it yields a sublimate of nitrophthalic anhydride, together with water; when suddenly heated, it clears and gives off nitrous vapours.

Nitrophthalic acid is dibasic, forming acid and neutral salts.

The *acid ammonium-salt*, $C^8H^4(NH^4)(NO^2)O^4.2H^2O$, is deposited on pouring a small quantity of nitric acid into the solution of the neutral salt, sometimes in prisms with pyramidal summits, but more often in hexagonal and rhomboïdal plates. It does not give off any water at 120°, but when heated till it begins to melt, it gives off water and is converted into nitrophthalimide (p. 632).

*Neutral ammonium-salt*, $C^8H^3(NH^4)^2(NO^2)O^4$.—When an ammoniacal solution of nitrophthalic acid is left to evaporate, it deposits chiefly shining laminæ of the acid salt; but among these are sometimes found thicker but smaller crystals of the neutral salt, which may be picked out with a pair of forceps. This salt crystallises in monoclinic prisms usually having their obtuse edges truncated. Angle $oP : \infty P = 103°$; $\infty P : \infty P =$ about 127°.

The solution of the neutral ammonium-salt forms with solution of barium-chloride, even when very dilute and boiling, a white crystalline precipitate; with the chlorides of strontium and calcium, white precipitates, not however from dilute solutions; with mercurous nitrate, nitrate of silver and nitrate of lead, white precipitates. It does not precipitate sulphate of magnesium, ferrous sulphate or cupric sulphate.

The *barium-salt*, $C^8H^3Ba''(NO^2)O^4$, is a light yellowish-white powder, anhydrous after drying at 130°. It is quite insoluble even in excess of boiling nitrophthalic acid.

The *neutral lead-salt* has not been obtained. On pouring acetate of lead into a solution of the ammonium-salt, a flocculent precipitate is formed which changes on boiling to a yellowish powder, insoluble in water, and consisting of a *basic salt*, $C^8H^3Pb''(NO^2)O^4.Pb''O$.

The *silver-salt*, $C^8H^3Ag^2(NO^2)O^4$, is a white precipitate, insoluble in water, and decomposing quickly, with emission of light, when strongly heated.

*Dinitrophthalic acid*, $C^8H^4(NO^2)^2O^4$.—When phthalic acid is treated with pure nitric acid, or with a mixture of nitric and sulphuric acids, a variable quantity of nitrophthalic acid is obtained, whilst some of the phthalic acid remains unaltered, and another portion is converted into a mixture of several new acids, one of which is the dinitrophthalic acid. This latter acid, together with the other new acids, is also obtained by the prolonged action of nitric acid on naphthalene and the chlorinated naphthalene. (Hugo Müller, Zeitschr. Ch. Pharm. 1863, p. 257.)

**Amidophthalic acid,** $C^8H^5(NH^2)O^4$.—This substance is prepared by the action of sulphydrate of ammonium on nitrophthalic acid, or more readily by the action of metallic iron and acetic acid on the latter acid. On bringing in contact a concentrated solution of nitrophthalic acid with iron and acetic acid, reaction soon sets in with elevation of temperature. The mass is to be kept for some time in a warm place, and after all action has ceased, the brown powder formed is separated as completely as possible from the metallic iron, and exposed for some time in a moist state to the action of air, in order to prevent ferrous oxide from entering into solution on the subsequent treatment with caustic ammonia. The resulting product is exhausted with warm ammonia, and the filtered solution is evaporated and exposed for some time to the heat of the water-bath. The amidophthalic acid cannot be precipitated from its ammoniacal solution by the addition of an acid; it is best to expel the ammonia by heat. On treating the remaining mass with water, part dissolves, which is to be again evaporated and exposed to heat. The insoluble dirty-yellow residue consists of impure amidophthalic acid, which is best dissolved in water or alcohol, and then treated with animal charcoal. On cooling, the amidophthalic acid crystallises out in the form of lemon-yellow fibrous crystals having a silky lustre.

Amidophthalic acid is very little soluble in *water* or *alcohol* at ordinary temperatures, but more so at an elevated temperature, forming greenish-yellow solutions which exhibit a most remarkable green fluorescence very much like that of uranium-salts. (See AMIDOTEREPHTHALIC ACID under TEREPHTHALIC ACID.)

Amidophthalic acid combines with acids and with alkalis. The hydrochloric acid compound forms colourless foliated crystals which in contact with water or moist air become yellow by losing their acid. The compound with sulphuric acid resembles the former.

On boiling for some time a solution of amidophthalic acid with *hydrochloric* or *sulphuric acid*, a new acid is formed, which is colourless, crystallises well, possesses a sweet taste and is readily soluble in water and alcohol. This new acid appears to be isomeric with the yellow amidophthalic acid. On treating nitrophthalic acid with zinc or tin and hydrochloric acid, no yellow amidophthalic acid is obtained, apparently because the hydrochloric acid present converts it, as soon as it is formed, into the soluble modification just mentioned.

Amidophthalic acid shows a peculiar deportment to caustic alkalis. *Caustic potash* dissolves the acid with facility to a pale yellow liquid which on evaporation yields a crystalline mass very soluble in water. Addition of an acid to this solution however does not precipitate the amidophthalic acid, as might be expected from its degree of solubility, but it will do so on mixing with sal-ammoniac and evaporating to dryness. —*Ammonia* dissolves amidophthalic acid with difficulty; the solution behaves like the potash-solution but deposits the acid again on evaporation.

On passing a current of *nitrous acid* into an alcoholic solution of amidophthalic acid, nitrogen is evolved and a granular brownish-red precipitate is formed, which is the analogue of Griess's diazobenzo-amidobenzoic acid (p. 292).

**Azophthalic acid,** $C^8H^5NO^4$.—On treating a solution of nitrophthalic acid with sodium-amalgam, no hydrogen is given off, but the solution gradually turns yellow and brown. The product of this reaction is to be saturated with acetic acid, which separates some resinous matter. On addition of hydrochloric acid, a yellow crystalline precipitate is formed, which after purification forms azophthalic acid. This acid is of an orange colour, and crystallises from dilute aqueous or alcoholic solution in well developed but small crystals of a deep orange colour. It dissolves very slightly in cold water, more so in alcohol, especially when warm.

The azophthalates are all coloured either yellow or orange.

The *potassium-salt* crystallises well and is very soluble in water.

The *ammonium-salt* resembles the former; it does not lose ammonia on being kept in a warm place for some time.

The *barium-salt* is a yellow crystalline precipitate.

Azophthalic acid appears not to form an ether on passing hydrochloric acid into its alcoholic solution.

This acid is the analogue of the azobenzoic acid which Strecker (Ann. Ch. Pharm. cxxix. 129) obtained by the action of sodium-amalgam on a solution of nitrobenzoate of sodium. (Hugo Müller.)

**Azoxyphthalic acid.** When an alcoholic solution of nitrophthalic acid is heated for some time with an alcoholic solution of potash, the mixture turns brown, and if treated in the way just mentioned under azophthalic acid, yields azoxyphthalic acid. This acid resembles the former, but has more of a lemon-yellow colour. It forms small prismatic crystals, and yields crystalline salts with most metals. (Hugo Müller.)

**PHTHALIC ANHYDRIDE.** $C^8H^4O^3$. *Phthalide. Pyroalizaric acid.*—Obtained by distilling phthalic acid. Sublimes in fine elastic needles, the transverse section of which is a rhombus of 52° and 128°. It dissolves slightly in cold water, more easily in boiling water, reproducing phthalic acid. It is very soluble in alcohol and ether, melts at 105°, and crystallises in a fibrous mass on cooling. It dissolves completely in aqueous ammonia, with considerable rise of temperature, and the solution yields on evaporation a mass of slender flexible needles, apparently consisting of phthalamic acid or phthalamate of ammonium.

*Trichlorophthalic anhydride*, $C^8HCl^3O^3$, is produced by distilling trichlorophthalic acid. It is colourless and crystallises in needles from fusion. It unites with ammonia, forming a salt which gives a white precipitate with nitrate of silver.

*Nitrophthalic anhydride*, $C^8H^3(NO^2)O^3$, is obtained, by subliming nitrophthalic acid at a gentle heat, in long white needles whose transverse section is a rhombus of 52° and 128°. It is very little soluble in water. (Laurent, Marignac.)

**PHTHALIC ETHERS.** The ethyl-, amyl- and phenyl-ethers, $C^8H^4(C^2H^5)^2O^4$, &c., are heavy oily liquids produced by the action of the corresponding alcohols on chloride of phthalyl (H. Müller). The ethylic ether is also produced by boiling the acid or anhydride with alcohol. (Laurent.)

**PHTHALIDE.** Syn. with PHTHALIC ANHYDRIDE.

**PHTHALIDINE.** $C^8H^9N = \left.\begin{matrix}C^8H^7\\H^2\end{matrix}\right\}N$. (Dusart, Ann. Ch. Phys. xlv. 335.)—A base produced by the action of sulphydric acid on nitrophthalene (p. 112), in the presence of alcohol and ammonia. A mixture of an alcoholic solution of nitrophthalene and sulphide of ammonium is heated to 50° for several hours in the water-bath; the greater part of the alcohol is distilled off; the remainder evaporated almost to dryness at a gentle heat; the residue extracted with dilute hydrochloric acid; and the filtrate saturated with potash. The precipitate is at first white and then redissolves in the acid solution with a beautiful blue colour; on adding an excess of potash, flesh-coloured flakes are formed, which gradually become denser and dark-coloured. The precipitate is washed on a filter with water, until the filtrate no longer exhibits an alkaline reaction; it then becomes crystalline.

Phthalidine crystallises from its aqueous solution after the lapse of a few days in beautiful needles. When melted and cooled, it forms a crystalline mass of the colour of realgar. It melts at about 22°, and when it solidifies, the thermometer rises to 34·5°. It smells like naphthalene, and tastes unpleasantly pungent. Its solutions do not restore the blue colour to red litmus, but its vapour (at what temperature?) turns it immediately blue. Very small quantities of phthalidine impart a beautiful blue colour to solutions of ferric salts. It is moderately soluble in cold *water*, and dissolves in all proportions in warm *alcohol* and *ether*.

Phthalidine begins to boil at 255°, but the thermometer rises very rapidly, while decomposition takes place, and a carbonaceous residue remains behind. It is converted into a yellowish-white mass by *chlorine-water*. It reduces *nitrate of silver*, the solution depositing very brilliant crystals. The aqueous solution produces a grey precipitate with *mercurous salts*, and a yellow precipitate with *ferrous salts*. It blackens on addition of *chloride of gold*. A solution of hydrochlorate of phthalidine is rapidly decomposed by *tetrachloride of platinum*, assuming a green colour, and depositing blue flakes which blacken on drying; a warm saturated solution of the salt forms with tetrachloride of platinum beautiful yellow crystals which partially decompose on drying.

The salts of phthalidine are soluble in water and in alcohol.

*Hydrochlorate*, $C^8H^9N.HCl$.—A warm alcoholic solution of the base saturated with hydrochloric acid immediately becomes filled with violet-blue crystals.

The *nitrate*, $C^8H^9N.HNO^3$, is formed in a similar manner.

*Sulphate*, $2C^8H^9N.H^2SO^4$.—Sulphuric acid unites directly with phthalidine and forms a dark green mass, which attracts moisture from the air and becomes blue. The crystallised salt is obtained by double decomposition, or by mixing the alcoholic solution of the base with sulphuric acid. It dissolves much less readily in alcohol than the other salts.

*Ethyl-phthalidine*, $C^{10}H^{13}N = C^8H^8(C^2H^5)N$, is a liquid having the odour of phthalidine, and distilling without decomposition. The *hydriodate*, $C^{10}H^{13}N.HI$, forms silvery flakes which give off iodine at 100° and turn yellow. The *hydrochlorate* is very similar. (Dusart.)

**PHTHALIMIDE.** $C^8H^5NO^2 = \left.\begin{matrix}(C^8H^4O^2)'' \\ H\end{matrix}\right\}N$. (Laurent, Ann. Ch. Phys. [2] lxi. 121; [3] xxiii. 119.)—This compound, isomeric with isatin, is formed by heating acid phthalate or phthalamate of ammonium:

$$\underset{\text{Acid phthalate.}}{C^8H^5(NH^4)O^4} \quad = \quad C^8H^5NO^2 \quad + \quad 2H^2O.$$

$$\underset{\text{Phthalamate.}}{C^8H^6(NH^4)NO^3} \quad = \quad C^8H^5NO^2 \quad + \quad H^2O \quad + \quad NH^3.$$

It is colourless; crystallises from ether by spontaneous evaporation in six-sided prisms derived from a rhomboïdal prism with angles of 113°. It melts when heated, and solidifies in a striated mass on cooling; at a stronger heat it boils and sublimes in very light flakes. It is inodorous and tasteless. It is insoluble in cold *water*, and slightly soluble in hot water; easily soluble in boiling *alcohol* and *ether*. It is not attacked by chlorine or by weak or diluted acids. It dissolves in strong *sulphuric acid* when heated, and if water is added to the solution, phthalic acid separates out on cooling. Boiled with an alcoholic solution of *potash*, it evolves ammonia, and forms phthalate of potassium.

*Silver-phthalimide*, $C^8H^4NAgO^2$.—A boiling alcoholic solution of phthalimide does not precipitate nitrate of silver, but on addition of ammonia it deposits a pulverulent precipitate or crystalline spangles, which dissolve in hot ammonia and crystallise out unchanged. The solution of the silver-salt in ammonia and a little hot water deposits needles which appear to consist of phthalamate of ammonium. When heated, it melts, swells up and forms a black mass, which at a higher temperature assumes a fine green colour, with golden lustre, like the wings of cantharides, phthalimide subliming at the same time. (Gerhardt, *Traité*, iii. 488.)

*Phenyl-phthalimide*, $C^{14}H^9NO^2 = \left.\begin{matrix}(C^8H^4O^2)'' \\ C^6H^5\end{matrix}\right\}N$.—On melting phthalic acid with aniline, and treating the cold pulverised mass with boiling alcohol, phenyl-phthalimide remains as a crystalline powder, which may be purified by sublimation and recrystallisation from boiling alcohol. It forms beautiful colourless needles, insoluble in water, melts at 203°, and begins to sublime in needles before fusion. With melting *potash* it yields aniline and phthalate of potassium. Boiling aqueous ammonia converts it into phenyl-phthalamic acid.

*Nitrophthalimide*, $C^8H^4N^2O^4 = \left.\begin{matrix}[C^8H^3(NO^2)O^2]''\\ H\end{matrix}\right\}N$, is produced by heating nitrophthalate of ammonium.

**PHTHALYL, CHLORIDE OF.** $(C^8H^4O^2)''Cl^2$. (H. Müller, Zeitschr. Ch. Pharm. 1863, p. 257.)—Phthalic acid or anhydride is readily acted upon by pentachloride of phosphorus, with evolution of hydrochloric acid and phosphoric oxychloride. The product is a heavy oily liquid of peculiar odour, resembling chloride of benzoyl. It distils at about 270° without decomposition, and does not solidify on cooling. It sinks in water, but soon becomes converted into phthalic acid. If kept in imperfectly closed vessels, it gradually deposits large crystals of phthalic anhydride. It acts with energy on the alcohols, forming the corresponding ethers (p. 631).

*Chloride of Nitrophthalyl* is prepared like the preceding, and resembles it in its properties, but cannot be distilled without decomposition.

**PHTHANITE.** (*Kieselschiefer.*) A flinty fissile variety of granular quartz having a grey, black, or greenish colour.

**PHYCIC ACID.** (Lamy, Ann. Ch. Phys. [3], xxxv. 129.)—An acid contained, together with phycite, in *Protococcus vulgaris*. It is extracted by alcohol, and separates therefrom by slow evaporation in bulky stellate groups of needle-shaped crystals, colourless, somewhat unctuous to the touch, tasteless, inodorous, and permanent in the air. Specific gravity = 0·898. It melts at 138°, solidifying to a silky crystalline mass on cooling; begins to boil at 150°, gradually decomposing and exhaling a characteristic odour. By distillation it yields oily products, insoluble in water, very soluble in alcohol. The acid is insoluble in water, but dissolves, especially when aided by heat, in *alcohol*, *ether*, *acetone*, and *oils* both fat and volatile: 1 pt. of it dissolves in 15 pts. of boiling absolute alcohol. The alcoholic solution is neutral.

Phycic acid gives by analysis 89·8—70·8 per cent. carbon, 11·7—12·0 hydrogen, and 3·7—3·8 nitrogen, besides oxygen; no formula has been proposed for it.

Phycic acid dissolves in strong *sulphuric acid*, and is reprecipitated by water. *Nitric acid* attacks it slowly, forming a light very acrid oil and a crystallisable acid. It is not attacked by dry *chlorine* even in sunshine. *Iodine* and *phosphorus* act upon it only at high temperatures. It is decomposed by heating with *potassium*, yielding hydrocyanic acid, together with other products. When heated with soda-lime, it gives off ammonia.

Ammonia has no action on phycic acid. *Potash* and *soda* dissolve it, forming salts which crystallise in needles, are neutral to test-papers, and dissolve in water and alcohol, forming solutions which froth like soap-water. Most of the other salts of phycic acid are insoluble. The *silver-salt* is white, and blackens on exposure to light.

**PHYCITE.** $C^4H^{10}O^4$. Syn. with ERYTHROMANNITE (ii. 504).

The term phycite has lately been extended by Carius (Ann. Ch. Pharm. cxxxiv. 71) to the series of tetratomic alcohols $\left.\begin{matrix}(C^nH^{2n+2})^{iv}\\ H^4\end{matrix}\right\}O^4$, homologous with natural phycite. He has obtained, by an artificial process, a 3-carbon alcohol, having the composition $\left.\begin{matrix}(C^3H^4)^{iv}\\ H^4\end{matrix}\right\}O^4$, and prepared several of its derivatives; but whether this alcohol is really homologous in constitution with native phycite, cannot be determined till the 4-carbon compound $C^4H^{10}O^4$ has also been obtained by a corresponding process, and its properties and reactions compared with those of natural phycite (see TRITYL-PHYCITE).

**PHYCOCYAN** and **PHYCOERYTHRIN.** These names are applied by Kützing to a blue and red colouring matter, apparently of the same composition, existing in several red sea-weeds. (Handw. d. Chem. vi. 495.)

**PHYCOHÆMATIN.** A red colouring matter, obtained by Kützing from *Rytiplæa tinctoria*. It is extracted from the fresh alga by maceration in cold water, and separates in flocks on evaporating the solution and adding alcohol. It is insoluble in ether and in oils. The colour is destroyed by exposure to sun-light, so that old specimens of the alga are often destitute of colouring matter. (Handw. *loc. cit.*)

**PHYLLIN GLANCE.** A mineral from Deutsch-Pilsen in Hungary, containing, according to Plattner, sulphur, antimony, tellurium, lead, and gold.

**PHYLLITE.** A mineral from Sterling, Massachusetts, resembling ottrelite (p. 248), and containing 38·40 per cent. silica, 23·88 alumina, 17·52 ferric oxide, 8·96 magnesia, 6·80 potash, and 4·80 water, a composition which may be represented by the formula $(Mg'';K^2)SiO^3.(Al^2;Fe^2)SiO^5.H^2O$ (*Rammelsberg's Mineralchemie*, p. 865).

**PHYLLOCHLOR.** Syn. with CHLOROPHYLL.

**PHYLLOCYANIN** and **PHYLLOXANTHIN.** These names are applied by Frémy to a blue and a yellow substance, of which he supposes chlorophyll to be composed. He separates them by agitating chlorophyll with a mixture of ether and hydrochloric acid, the yellow substance then dissolving in the ether, and the blue in the hydrochloric acid (Frémy, Compt. rend. l. 405; Jahresb. 1860, p. 533). According to H. Ludwig, also (Arch. Pharm. [2] cvi. 164; Jahresb. 1861, p. 738), when chlorophyll (from young wheat-leaves) is boiled with strong alcoholic potash, and the solution is neutralised with hydrochloric acid, a yellow precipitate is formed, together with a splendid blue liquid, which leaves phyllocyanin, on slow evaporation, as a dark blue mass. Stokes, on the other hand, concludes, from the fluorescent and absorbent properties of chlorophyll, that it does not contain a blue substance, and that Frémy's phyllocyanin is a product of the decomposition of chlorophyll by acids. (Chem. Soc. J. xvii. 314.)

**PHYLLORETIN.** A fossil resin found, together with tekoretin, in the fossil wood of Denmark. It melts at 86°—to 87°, dissolves easily in alcohol, and appears to have the composition $C^8H^{10}$. (Forchammer, J. pr. Chem. xx. 459.)

**PHYLLOXANTHEÏN.** A yellow substance, produced, according to Frémy (*loc. cit.*), by the action of bases on chlorophyll, or on phyllocyanin. It is reconverted into phyllocyanin by the action of acids.

**PHYLLOXANTHIN.** The yellow substance pre-existing in chlorophyll. The mode of separating it from the blue constituent by the action of ether and hydrochloric acid, or alcoholic potash and hydrochloric acid, has already been mentioned. It may also be obtained by adding hydrate of aluminium to an alcoholic solution of chlorophyll diluted with a considerable quantity of water. The whole of the colouring matter is then precipitated as a yellowish-green alumina-lake, from which the phylloxanthin may be extracted by sulphide of carbon, leaving the lake of a more bluish-green colour. (Frémy.)

**PHYSALIN.** $C^{14}H^{16}O^5$. (Dessaignes and Chantard, J. Pharm. [3] xxi. 24 ) The bitter principle of the winter cherry (*Physalis alkekengi*), a solanaceous plant growing in the south of Europe, sometimes used as a substitute for quinine in the treatment of intermittent fevers.

It is prepared by briskly agitating the aqueous extract of the leaves with chloroform, which deposits it after long standing; and is purified by dissolving it in hot alcohol, with addition of a little charcoal, precipitating the filtered liquid with water, and washing the precipitate with cold water on a filter.

Physalin is a light perfectly amorphous powder, having a yellowish colour and a bitter taste, slight at first, but afterwards strong and persistent. When dry, it becomes strongly electric by friction. It is very slightly soluble in cold water and in ether, somewhat more in boiling water, easily in chloroform and in alcohol, especially the latter. When heated, it softens at about 180°, and decomposes at a higher temperature. It is but slightly soluble in acids, moderately soluble in ammonia, but the alkali is all driven off on evaporation. The alcoholic solution does not precipitate ammoniacal nitrate of silver, but gives a white precipitate with acetate of lead and ammonia.

**PHYSALITE** or *Pyrophysalite.* A coarse nearly opaque variety of topaz, found in yellowish-white crystals, which intumesce when heated: hence its name (from *φυσάνειν*, to blow). It occurs in crystals of great size at Fossum in Norway; at Finbo, Sweden, in a granite quarry, and at Braddbo, in a boulder; one crystal from the last locality, at Stockholm, weighs eighty pounds.

**PHYSETOLEIC ACID.** $C^{16}H^{30}O^2$.—A fatty acid discovered by Hofstädter (Ann. Ch. Pharm. xci. 177) in sperm oil; isomeric if not identical with hypogæic acid, obtained from the oil of *Arachis hypogæa* (iii. 238).

To prepare it, the soap obtained by boiling the oil with potash-ley is dissolved in boiling alcohol; and the filtrate, after being freed from alcohol by distillation, is diluted with water, and reprecipitated by ammoniacal sugar-of-lead. The precipitate, washed by decantation and dried in the air, is drenched with ether, which dissolves physetoleate of lead and undecomposed spermaceti, leaving undissolved the lead-salts of the solid fatty acids. The solution is separated; part of the ether is distilled off; the residue decomposed by hydrochloric acid; the ethereal solution is mixed with ammonia and chloride of barium; the precipitate is collected, washed, and dried in a vacuum; and the ethal and spermaceti are removed from it by cold ether. On repeatedly boiling the undissolved physetoleate of barium with alcohol of 93 per cent., and cooling the resulting solutions separately, the portion taken up is deposited as a white powder, which must be collected out of contact with the air, washed with alcohol, and immediately dried in a vacuum. It may be obtained pure by recrystallising it twice more in the same way, and decomposed by boiling with aqueous tartaric acid.

Physetoleic acid crystallises in stellate groups of colourless needles; it is inodorous, melts at 30°, and solidifies at 28° (hypogæic acid from earth-nut oil melts at 34° or 35°). In its reactions and combinations it exactly resembles hypogæic acid.

**PHYSODIN.** $C^{12}H^{12}O^{8}$. (Gerding, N. Br. Arch. lxxxvii. 1.)—A neutral substance occurring in *Parmelia ceratophylla*, var. *physodes* (also called *Parmelia physodes*). To obtain it, the lichen air-dried and cut in pieces is macerated with ether for several days; the ether is evaporated; and the residual white powder is purified by washing it with alcohol, and repeated crystallisation from absolute alcohol.

It forms a white loosely coherent mass, appearing when magnified 120 times to consist of four-sided truncated prisms. It melts at 125°. Dried at 100°, it gives by analysis (mean) 49·75 per cent. carbon and 4·63 hydrogen, the formula requiring 50·70 carbon, 4·28 hydrogen, and 45·07 oxygen.

Physodin behaves to *water* like a resin, not being wetted thereby. It dissolves in *alcohol* of 80 per cent., but is insoluble in absolute alcohol, in ether, and in acetic acid. It is not altered by dilute acids. It dissolves easily in warm aqueous *ammonia*, forming a yellow solution which becomes reddish on exposure to the air. In *carbonate of ammonia* it dissolves slightly at ordinary temperatures, easily on boiling; in *potash* instantly with yellow colour. Acids precipitate from these solutions light yellow or reddish flocks; the potash-solution yields a dingy-yellow precipitate with *chloride of barium*. The alcoholic solution is not precipitated by chloride of barium, but yields with *acetate of lead* a pale yellow precipitate soluble in potash; with *cupric sulphate* a pale green; and with *nitrate of silver* a brown-red precipitate.

ADDENDUM. *Ceratophyllin* (O. Hesse, Ann. Ch. Pharm. cxix. 365).—This substance occurs, together with physodin, in *Parmelia ceratophylla*, var. *physodes*. To prepare it, about 3 lbs. of the lichen, after being washed with water, is stirred up with clear lime-water; the alkaline solution is neutralised with hydrochloric acid; and the resulting yellowish-grey flocculent precipitate is washed several times with cold water to remove the excess of acid, then collected, dried in the air, and freed from uncrystallisable matter by digestion with boiling alcohol of 75 per cent. There then remains a dark green, soft, elastic mass, probably containing physodin and usnic acid, to remove which, the mass is boiled with strong soda-ley. A dark brown liquid is thus obtained, which, on cooling, deposits ceratophyllin unmixed with either of the substances just mentioned. It may be separated from the mother-liquor by filtration, and purified by recrystallisation from boiling alcohol with the aid of animal charcoal. When the lichen, without previous washing, is stirred up with thin milk of lime, the yellowish filtrate does not yield any precipitate with hydrochloric acid. The precipitate formed as above described is particularly abundant when the lichen has been obtained from birch-stems, and the maceration has not been continued for more than 15 hours.

Ceratophyllin forms thin white prisms, which when placed upon the tongue, produce, at first, a slightly irritating taste, soon becoming rather strongly perceptible in the throat; subsequently a persistent burning sensation is experienced on the tongue. It melts at 147° to a colourless liquid, and solidifies in the crystalline form between 136° and 138°. It begins to sublime even at the melting point, and at a somewhat higher temperature sublimes very easily and without alteration, in thin colourless laminæ.

Ceratophyllin appears to be a higher homologue of orsellinate of ethyl, $C^{10}H^{12}O^{4}$; its melting point is about 15° higher than that of the latter.

Ceratophyllin is much more soluble in hot *water* than in cold; it dissolves readily in *alcohol*, *ether*, *potash-ley*, *aqueous ammonia*, and *lime-water*. The alcoholic solution, which has a neutral reaction, is coloured purple-violet by a small quantity of *ferric chloride*, blood-red by solution of *chloride of lime*, the latter colour being destroyed by excess of the reagent; no precipitate with alcoholic sugar-of-lead or nitrate of silver. From the ammoniacal solution *hydrochloric acid* throws down the ceratophyllin in thin prisms. Ceratophyllin dissolves in dilute *nitric acid*, the solution acquiring only a slight yellow tint when heated. Strong *sulphuric acid* dissolves it without alteration at ordinary temperatures, but chars it when heated.

**PHYSOSTIGMINE.** (J. Jobst and O. Hesse, Ann. Ch. Pharm. cxxix. 115; Jahresb. 1864, p. 454.)—An alkaloïd obtained from the Calabar bean, the seed of *Physostigma venenosum*, a poisonous leguminous plant growing in marshy situations near Attarpah and Old Calabar in Upper Guinea. The poisonous power appears to reside only in the cotyledons. By repeatedly exhausting the shelled beans with boiling alcohol of 80 per cent., and evaporating the extract, a yellowish residue is obtained, which dissolves in water with acid reaction, and separation of a small quantity of oil. Neutral acetate of lead added to this solution throws down an acid (not precipitable by lime-water, chloride of calcium, or nitrate of silver), and the filtrate freed from lead by sulphydric acid, yields on evaporation a red residue, from which absolute alcohol extracts acetate of physostigmine, leaving gum undissolved.

The base itself is most easily prepared from the extract by saturating its solution in a small quantity of cold water with calcined magnesia, evaporating, and treating the still moist residue with ether, as long as that solvent takes up any of the base. The ethereal solution is agitated with a few drops of very dilute sulphuric acid; the lower dark red layer of liquid is again shaken up with magnesia; the base thus separated is dissolved up by ether; and the solution is left to evaporate.

Physostigmine thus obtained is a brownish-yellow amorphous mass, sparingly soluble in water, moderately soluble in ether, alcohol, benzene, ammonia, and soda. From the ethereal solution it is completely precipitated by animal charcoal. The aqueous solution has a slight burning taste, a distinct alkaline reaction, forms a kermes coloured precipitate with iodide of hydrogen and potassium, and precipitates ferric hydrate from a solution of the chloride.

The solutions of physostigmine in acids have a dark red or more rarely a dark blue colour; they are more or less decolorised by sulphydric acid, and leave the salts in the form of red amorphous masses, easily soluble in water and in alcohol. They form amorphous precipitates with *tannic acid* and with *platinic*, *auric* and *mercuric chlorides*. The *gold-salt* decomposes easily, with separation of the metals.

Physostigmine is the active principle of the Calabar bean. The solution given in small doses to a rabbit produces paralysis in five and death in twenty minutes, without contraction of the pupils. When dropt into the eye, however (even an hour after death), it produces in ten minutes considerable contraction of the pupil. According to Christison, a dose of 0·8 grm. of the bean produces vertigo, and strong paralysis of the voluntary muscles without any painful symptoms; according to Harley, a piece of the size of a millet-seed will kill a cat or a rabbit; according to Robertson, the bean produces transient contraction of the *Sphincter Iridis* and *Musculus ciliaris*, and therefore affords an excellent means of counteracting dilatation of the pupil. The alcoholic extract of the beans is the most convenient for medical purposes.

**PHYTOCHEMISTRY.** The Chemistry of Plants. The most comprehensive treatise on this subject is that of Rochleder, published at Leipzig in 1854, and given in a somewhat abridged form in the eighth volume of Gmelin's "Handbuch der Chemie," containing: 1. The proximate principles of plants arranged according to orders and genera.—2. The nutrition of plants, and the formation and metamorphoses of their several constituents. See also the articles, ASH OF ORGANIC BODIES, MANURE, and NUTRITION OF PLANTS in this Dictionary; also the several articles describing the chemical constitution of individual plants.

**PHYTOMELIN** or *Plant-yellow*. A name proposed by W. Stein for rutin, on account of its wide diffusion in the vegetable kingdom. (See RUTIN.)

**PIANZITE.** An earthy resin occurring at Pianze near Neustadt in Carniola, in brownish-black masses with yellowish-brown streak. Hardness = 1·5. Specific gravity = 1·220. It melts at 315°, and burns with an aromatic odour and much smoke, leaving 5·96 per cent. ash. It dissolves in ether and in caustic potash, freely also in absolute alcohol. When heated in a glass tube, it yields a yellowish oily distillate having an acid reaction. (Haidinger, Pogg. Ann. lxii. 275.)

**PICAMAR.** One of the products of the distillation of wood-tar. It is an oil of specific gravity 1·10, unctuous to the touch, having a faint odour and a burning bitter taste. It boils at about 270°, and unites with alkalis, forming crystallisable compounds. (Reichenbach.)

**PICHURIC ACID.** Syn. with LAURIC ACID (iii. 473).

**PICHURIM-OIL.** Pichurim-beans, *Fabæ Pichurim minores* (from *Ocotea pichury minor*, Martius), yield by distillation with water, a yellow oil, smelling like bay and sassafras oil, and having a sharp burning taste. By distillation with sulphuric acid (which prevents the beans from aggregating into a pasty mass, and increases the yield of liquid), Müller (J. pr. Chem. lviii. 463) obtained a yellowish-green oil, having the peculiar odour of the beans, slightly soluble in aqueous alcohol, easily soluble in absolute alcohol and in ether. By repeated fractional distillation, it may be resolved into a number of oils of constant boiling point, viz. (1). A colourless mobile oil boiling at 150°, and emitting, when rubbed between the fingers, a very pungent odour like that of the leaves of *Teucrium Marum*.—(2). A transparent colourless oil boiling between 165° and 170°, and smelling like oranges when its vapour mixes with the air in small quantity, like turpentine in larger quantity. Both these oils, after drying over chloride of calcium and solid potash, consist essentially of a hydrocarbon $C^5H^8$, partly altered by oxidation.—(3). A yellowish-green oil boiling between 235° and 240°, smelling like the beans, more viscid than the preceding, and agreeing nearly in composition with the empirical formula $C^{28}H^{38}O^2$.—(4). In larger quantity, an oil boiling between 260° and 265°, and agreeing nearly in composition with the formula $C^{28}H^{18}O$. This oil has a faint odour and deep blue colour permanent in the dark, but changing to greenish-yellow under the influence of light or of oxidising agents, appearing then to be converted into that last described.

*Pichurim-camphor.* According to Bonastre, pichurim-oil is resolved by cold alcohol into a strong-smelling elæoptene and a nearly inodorous camphor or stearoptene which separates in white shining micaceous laminæ. According to Müller, the dark blue oil above mentioned deposits crystals of lauric acid, which may be extracted in larger quantity by means of soda. Bonastre's camphor perhaps consisted either of this acid or of laurostearin.

**PICHUROSTEARIC ACID.** Syn. with LAURIC ACID.

**PICKERINGITE.** Native magnesia-alum found near Iquique in Peru (see SULPHATES).

**PICOLINE.** $C^6H^7N$. *Odorine.* (Unverdorben, Pogg. Ann. viii. 259, 480; xi. 59.—Anderson, N. Ed. Phil. J. xli. 146, 291; Phil. Mag. J. [3] xxxiii. 185; also J. pr. Chem. 45, 166; Ed. Phil. Trans. xxi. Pt. 1, 219; Phil. Mag. J. [4] ix. 214; also Ed. Phil. Trans. xxi. Pt. 4, 578.—C. Greville Williams, Chem. Soc. Qu. J. vii. 97; Chem. Gaz. xii. 283; Ed. Phil. Trans. xxi. Pt. 2, 313; Church and Owen, Chem. News, ii. 146.—Wertheim, Ann. Ch. Pharm. lxx. 62; Chem. Gaz. vii. 309.)

In 1826, Unverdorben, while investigating the fœtid oil obtained in the destructive distillation of bones, discovered several volatile alkaloïds. Among these was one distinguished by its overpowering and persistent smell; to this substance he gave the name of *odorine.* The experiments of Unverdorben however, although conducted with remarkable skill and perseverance, did not in any way establish the composition of the bodies which he separated, and as no salt was obtained by him free from other homologues of the same series, we shall not, except in special cases, quote his results. Most of the facts observed by him may be found in Gmelin's *Handbook*, xi. 263 *et seq.* But in 1846, Dr. Anderson succeeded in isolating a base from coal-naphtha, which he showed to be isomeric with aniline. He also showed its relations to Unverdorben's odorine, and gave it the name of picoline. Subsequently he detected the same alkaloïd in bone-oil, accompanied by numerous homologues, including pyridine, the first member of the series.

*Occurrence and Formation.*—1. In coal-naphtha (Anderson).—2. In bone-oil (Anderson).—3. In the tar produced by distilling the bituminous slate of Dorsetshire (Williams).—4. It is probably contained in the basic liquid obtained by Stenhouse in his researches on the products of the destructive distillation of beans, &c.—5. A base possessing the same centesimal composition and boiling point is found among the products of the distillation of cinchonine (Williams).—6. In the distillate from peat (Church and Owen). The statement by Wertheim that picoline is yielded by piperine when distilled with soda-lime is erroneous. The base obtained in that manner is piperidine, $C^5H^{11}N$. The question of the identity or isomerism of the tertiary monamines formed during destructive distillation is one of the greatest difficulty, and recent researches have shown not only that the chinoline and leucoline series are distinct, but also that the pyridine series, as found in the distillate from cinchonine, also form a distinct class. (See LUTIDINE, iii. 737.)

*Preparation.*—The preparation of all volatile bases (except pyrrol) from the oily products of destructive distillation, is conducted in nearly the same manner. The oils are first to be shaken up with sulphuric acid diluted with about twice its weight of water. This treatment with acid may be repeated to ensure the entire removal of the last portions of the bases. On standing, the acid solution settles to the bottom of the vessel and may be removed by means of a siphon or separator. A very good apparatus for the purpose consists of a carboy from which the bottom has been removed. It is to be inverted and placed on any convenient support which will allow of vessels being placed beneath. A sound bung to which a stopcock has been fitted is then to be cemented to the neck of the carboy. The mixture having been placed in the separator the acid liquid is to be drawn off below. The next step is to boil in an open vessel as long as pyrrol is given off. This may be ascertained by holding a slip of fir-wood, moistened with strong hydrochloric acid, in the escaping steam. When the wood is no longer reddened the boiling may be stopped. If it be desired to save the pyrrol the operation must be conducted in a still. As soon as the pyrrol has been expelled, the liquid is to be strained through calico to remove pitchy and resinous matters. An excess of caustic soda is then to be added, and the whole distilled as long as the distillate contains bases. This may be ascertained by seeing whether fumes are given off on the approach of a rod dipped in hydrochloric acid. If the distillate is very weak, it is to be concentrated by a second distillation, before proceeding to the next operation. The next step is to add a large excess of solid potash to the liquid, so as to render the bases insoluble, and cause them to rise to the surface. This operation must be performed with care, in order to prevent the temperature rising sufficiently to cause a loss of the more volatile constituents.

The basic oil which rises to the surface after the addition of the solid potash, is to be separated from the aqueous liquid, and placed in bottles of moderate size. The mixture of bases still contains a large quantity of water, which must be entirely removed before proceeding to the next operation. To effect this, sticks of potash are to be added and the whole allowed to stand a few minutes. The water will soon begin to act on the potash, and the solution of hydrate of potassium which sinks to the bottom of the bottles is to be removed as fast as it is formed. The most convenient mode of doing this is by means of a large pipette furnished with a vulcanised india-rubber ball at its upper extremity. The ball is to be pressed flat in the hand, and the lower end of the pipette being immersed in the liquid to be removed, the pressure on the ball is to be lessened; the liquid will then enter the bulb of the pipette and may, after removal, be expelled by renewing the pressure. After proceeding as above for about half an hour, it will generally be found that the separation of the water will begin to take place very slowly. More solid potash is then to be added and the whole left at rest for some hours; the removal of the aqueous portion is then to be repeated. It will require a day or two of digestion to effectually remove every trace of moisture. It will also be found that the more volatile and soluble in water the bases are, the more digestion will be required. It must not be forgotten that if aniline and its homologues are present, they must be destroyed by boiling with nitric acid before attempting the dehydration.

It is absolutely essential to remove every trace of moisture before proceeding to fractional distillation. The smallest quantity of water will give rise to the greatest errors if it be attempted to separate mixtures by taking advantage of the differences in the boiling points of the substances present. The whole liquid will now require to be subjected to a complete and systematic distillation. This process is exceedingly tedious and takes a vast amount of time. A mixture containing six or eight homologous bases will require thirteen or fourteen complete fractionations, involving nearly a thousand distillations, before anything approaching to complete separation will be effected. For full details of the methods of conducting the operation, the reader is referred to the original memoirs quoted at the head of this article.

The picoline will be found in the fractions boiling at about 135°. The fractions distilling in the twelfth or thirteenth rectifications between 130° and 140° will consist of almost pure picoline.

*Properties.*—Picoline is a colourless mobile liquid which does not freeze at 0°. It has an intensely powerful and characteristic odour, and when inhaled through the nostrils, produces a bitter taste in the mouth and back of throat. It fumes strongly on the approach of a rod dipped in hydrochloric acid. It blues litmus but does not affect the colour of a solution of red cabbage. It does not yield any coloured reaction when chloride of lime is added to its aqueous solution, but the mixture acquires a new and peculiar odour. It boils steadily at about 135° (Anderson). Its specific gravity at 0° is 0·9613. The density of its vapour was found by experiment to be 3·290. Theory requires 3·224. The refractive indices of a specimen prepared from peat by Mr. Church, and having a specific gravity of 0·955, were found by Gladstone and Dale to be for A, 1·4888; D, 1·4980; H, 1·5314, the temperature at the time being 22·5°. (Phil. Trans. 1863, p. 317.)

*Decompositions.*—1. The action of *chlorine* on picoline varies according to the manner in which the experiment is made. When a current of the gas is passed through an aqueous solution, absorption takes place, the liquid becomes brown, and a peculiar pungent odour is evolved. From the solution potash precipitates a dark brown resinous matter. But if excess of picoline be poured into a bottle of chlorine, and the liquid be distributed over the surface of the bottle, the greater portion is converted into a crystallised mass, which, on treatment with water, leaves an amorphous powder of dazzling whiteness. It is insoluble in water but soluble in alcohol. It consists of the hydrochlorate of trichloropicoline, $C^6H^4Cl^3N^3.HCl$ (Anderson).—2. *Bromine-water* added to solution of picoline yields a resinous precipitate, insoluble in water, but soluble in alcohol and ether. When picoline is thrown into a vessel filled with bromine-vapour, the reaction which ensues is analogous to that with chlorine.—3. *Iodine* in presence of water yields hydriodate of picoline mixed with a brown impurity.—4. *Nitric acid* does not readily decompose picoline even when boiled; no picric acid is formed even after prolonged ebullition. Nitric acid in the cold yields nitrate of picoline (Anderson).—5. *Sodium* cohobated for some days with picoline converts it into parapicoline, a new and remarkable base apparently polymeric with picoline itself. Its formula is $C^6H^7N.C^6H^7N = C^{12}H^{14}N^2$. It boils between 260° and 316°, and is at the same time partially decomposed, with formation of pyrrol and carbonate of ammonium. It must be distilled in a current of hydrogen at a temperature below its boiling point. (Anderson.)

Picoline-salts.—Picoline unites with acids forming salts, most of which are exceedingly soluble, but in general crystallisable when carefully prepared. On mixing them with strong acids considerable heat is evolved. All picoline-salts are readily decomposed by fixed alkalis, with separation of the base. They closely resemble the salts of pyridine.

*Hydrochlorate.*—Hydrochloric acid and picoline mixed in the proportion of one equivalent of each and carefully evaporated on the water-bath, yield prismatic crystals, which sublime when gently heated. The sublimed salt is deliquescent. (Anderson.)

*Chlorocuprate of Picoline.*—Large rhombohedral crystals obtained by evaporating cupric chloride with hydrochlorate of picoline.

*Chloromercurate*, $C^6H^7N.Hg''Cl^2$.—Picoline added to a strong solution of corrosive sublimate yields a curdy precipitate. From dilute solutions it may be obtained in needles. The salt must be air-dried as it evolves picoline when heated. (Anderson.)

*Chloroaurate.*—Delicate yellow needles dissolving in 20 pts. of boiling water. (Unverdorben.)

*Chloroplatinate*, $2(C^6H^7N.HCl).Pt^{iv}Cl^4$.—This salt varies in appearance with the mode of preparation. A concentrated solution of tetrachloride of platinum added to a strong solution of hydrochlorate of picoline, yields orange-yellow needles requiring about 4 pts. of boiling water for solution. (Anderson.)

The platinum-salt is slowly decomposed by boiling with water, and yields, after eight or ten days, an insoluble substance resembling flowers of sulphur, and having the formula $C^{12}H^{16}Pt''N^2.4HCl$. It is the salt of a platinum-base analogous to platinamine; it is, therefore, the dihydrochlorate of platinopicoline. If the ebullition of the original platinum-salt with water be arrested at a certain point, which is only ascertainable by experiment, a double salt crystallises out containing 1 at. dihydrochlorate of platinopicoline united to 1 at. chloroplatinate of picoline. (Anderson.)

*Sulphate of Picoline.*—A neutral sulphate of picoline has not yet been obtained, owing to the tendency of the base to escape. When an excess is added to the acid, and the mixture is evaporated on the water-bath, the base continues to fly off until an acid salt is formed, which on cooling soldifies to a mass of colourless deliquescent crystals. (Anderson.)

*Oxalate of Picoline.*—When excess of picoline is added to solution of oxalic acid, and the mixture is evaporated over lime, the whole eventually solidifies to a dense crystalline mass, very soluble in water and alcohol. Heated to 100° it melts giving off picoline and yielding an acid salt. (Anderson.)

### *Substitution-derivatives of Picoline.*

*Hydriodate of Ethyl-picoline*, $C^8H^{11}N.HI = C^6H^6(C^2H^5)N.HI$.—Picoline is to be mixed with excess of iodide of ethyl, and sealed in glass tubes. On heating to 100° in a water-bath, combination begins to take place almost immediately, heat is evolved, the liquid separates into two layers, and in a few minutes the reaction is completed. On cooling, the upper stratum solidifies to a crystalline mass, and crystals also form in the lower layer which consists principally of the excess of iodide of ethyl. The solid and liquid portions are to be thrown on a filter, and the crystals washed with a mixture of alcohol and ether; after draining, the salt is to be dissolved in as small a quantity as possible of a boiling mixture of alcohol and ether. As the liquid cools the new substance is deposited in beautiful silvery plates. It is very soluble in water and alcohol, but less soluble in ether. (Anderson.)

*Ethyl-picoline.*—When the hydriodate is dissolved in water and moist oxide of silver is agitated with it, iodide of silver is precipitated and the base remains in solution. Heat must be avoided as the base is readily decomposed. If the operation be cautiously performed, a colourless solution results; it has a faint but peculiar odour, and is highly alkaline. It restores the blue of reddened litmus, turns turmeric brown, has a powerfully caustic taste, and feels soapy between the fingers. It reacts with metallic salts generally like potash or soda. On boiling, the solution becomes red, and ethylamine is evolved. (Anderson.)

*Platinum-salt of Ethylpicoline*, $2(C^8H^{11}N.HCl).PtCl^4$.—Orange-red tabular crystals of considerable size and great beauty. (Anderson.)

*Gold-salt*, $C^8H^{11}N.HCl.AuCl^3$.—Golden-yellow flattened prisms.

***Ethylene-dipicolyl-diammonium***, $C^{14}H^{18}N^2 = (C^2H^4)''(\overset{\prime\prime\prime}{C^6}H^7)^2N^2$.—The chloride or bromide of this base is obtained by treating picoline with chloride or bromide of ethylene: *e.g.*,

$$2(C^6H^7)'''N \quad + \quad C^2H^4Cl^2 \quad = \quad (C^2H^4)''(\overset{\prime\prime\prime}{C^6}H^7)^2N^2Cl^2.$$

(Church and Owen); see also Davidson (Chem. Soc. Qu. J. xiv. 165).

### *Constitution of Picoline.*

Picoline is a tertiary monamine, formed on the type of one atom of ammonia. But it differs from the tertiary monamines produced by the action of the iodides of the alcohol-radicles on ammonia, inasmuch as, instead of having the three atoms of hydrogen in the type replaced by three atoms of a radicle, they appear to be replaced by one triatomic radicle. It is therefore usual to write its formula $(C^6H^7)'''N$.

Nothing certain is known of the nature of any of the triatomic radicles contained in the tertiary monamines produced by destructive distillation. C. G. W.

**PICOLITE.** A black chromiferous spinel, occurring as an accessory constituent in Lherzolite (iii. 585). It has a density of 4·08, and contains, according to Damour's analysis (Jahresb. 1862, p. 724), 56·0 per cent. alumina, 8·8 chromic oxide, 10·3 magnesia, 24·0 ferrous oxide, and 2·0 siliceous residue (= 101·2).

**PICRAMIC ACID.** $C^6H^5N^2O^3$.—An acid produced by the action of reducing agents on picric acid (see NITROPHENAMIC ACIDS, p. 406).

**PICRAMMONIUM.** $C^6H^{12}N^3 = \left.\begin{matrix}(C^6H^3)'''\\ H^3\end{matrix}\right\}N^3$. Lautemann, Ann. Ch. Pharm. cxxv. 1.)—A tri-ammonium, the iodide of which is produced by the action of iodine and phosphorus on aqueous picric acid, that is, of hydriodic acid on picric acid:

$$C^6H^3(NO^2)^3O \ + \ 23HI \ = \ C^6H^{12}N^3I^3 \ + \ 7H^2O \ + \ 10I^2.$$

A saturated solution of picric acid, treated with iodine and phosphorus (best with 100 pts. iodine to about 20 pts. phosphorus), becomes heated to the boiling point, and on subsequently distilling off the excess of hydriodic acid in an atmosphere of carbonic anhydride, the remaining liquid solidifies, at a certain degree of concentration, to a mass of long yellowish needles of the tri-iodide, which may be obtained nearly colourless by washing with alcohol containing ether, solution in absolute alcohol, and evaporation in a vacuum over oil of vitriol.

Iodide of picrammonium is deliquescent and becomes resinous on exposure to light; crystallises from aqueous hydriodic acid, but not from water; from the alcoholic solution it is precipitated in the resinous state by ether. The aqueous solution reduces *platinic chloride*; forms a steel-blue precipitate with a strong solution of *ferric chloride*; and imparts to a dilute solution a deep blue colour, which changes to violet after a while, and then disappears, a flocculent precipitate separating at the same time. *Nitrate of silver* added to the solution of the iodide throws down silver-iodide and metallic silver, the supernatant liquid turning blue. The iodide evaporated with *nitric acid*, gives off a small quantity of gas, and yields brown crystals forming a blue solution in water. With *potash-ley* it gives off ammonia, and deposits brown flocks. The dilute solution of the iodide, mixed with a little *ammonia*, becomes blue; the concentrated solution acquires a transient dark-green colour.

Picramine, or hydrate of picrammonium, cannot be isolated on account of its ready oxidability.

*Acid Sulphate of Picrammonium*, $(C^6H^{12}N^3)'''H(SO^4)^2 = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^2\\ (C^6H^{12}N^3)'''\\ H\end{matrix}\right\}O^4$, is obtained by mixing the solution of the iodide in absolute alcohol with dilute sulphuric acid, in greyish-white flocks, which crystallise with partial decomposition from water. The sulphuric acid is completely precipitated from this salt by chloride of barium.

*Sulphato-iodide of Picrammonium*, $(C^6H^{12}N^3)'''\left\{\begin{matrix}(SO^4)''\\ I\end{matrix}\right..2H^2O = \begin{matrix}(SO^2)''\\ (C^6H^{12}N^3)'''\end{matrix}\left\{\begin{matrix}O^2\\ I\end{matrix}\right..2H^2O$, is obtained in light, amber-yellow, octahedral crystals, when the aqueous solution of the iodide, mixed with dilute sulphuric acid, is left to evaporate. It is easily soluble in water, nearly insoluble in alcohol and ether, and difficult to crystallise from water.

*Acid Phosphato-iodide of Picrammonium*, $\left.\begin{matrix}(C^6H^{12}N^3)'''(PO^4)'''\\ H \qquad\qquad I\end{matrix}\right\}.2H^2O = \left.\begin{matrix}(PO)'''\\ (C^6H^{12}N^3)'''\\ H\end{matrix}\right\}\begin{matrix}O^3\\ I\end{matrix}.2H^2O$, separates in the crystalline state on mixing the aqueous iodide with orthophosphoric acid. It dissolves easily in water, with difficulty in alcohol and ether. Phosphoric acid added to the alcoholic solution throws down an insoluble salt free from iodine, the solution of which in hydrochloric acid deposits needles having a satiny lustre.

**PICRAMYL.** The name applied by Berzelius to stilbene or hydride of stilbyl (see STILBENE).

**PICRANALCIME.** A mineral occurring in geodes in the gabbro of Tuscany; also in the steatitic paste of a metalliferous dyke. It forms trapezohedrons and cubo-trapezohedrons, with distinct cubic cleavage. Hardness = 5. Specific gravity = 2·257. Colour, flesh-red to colophonite-red. Lustre, vitreous. Contains, according to Bechi (Sill. Am. J. [2] xiv. 62), 59·11 per cent. silica, 22·08 alumina, 10·12 magnesia, 0·45 soda, 0·02 potash, and 7·67 water (= 99·45), agreeing with the formula $\left.\begin{matrix}Na^2O\\Al^2O^3\end{matrix}\right\}4SiO^2.H^2O$, which is that of analcime (i. 210) having the greater part of the sodium replaced by magnesium. The mineral has most probably been formed from analcime by the action of water containing magnesia. (Dana, ii. 318.)

**PICRANISIC ACID.** The name applied by Cahours to picric acid obtained by the action of potash on trinitranisol, which he supposed to be an isomeric modification; but it has since been shown to be identical with picric acid obtained from other sources (p. 402).

**PICRIC ACID.** $C^6H^2(NO^2)^3O$.—Already described as trinitrophenic acid (pp. 400–405).

**PICRIN.** A bitter substance, of doubtful constitution, obtained by Radig from fox-glove (*Digitalis purpurea*). It is described as a yellow-brown, sometimes crystalline substance, soluble in water, alcohol, and ether, and precipitated from the aqueous solution by mercuric chloride, ferrocyanide of potassium, and acetate of lead, not by carbonate of potassium, or sulphate of copper (Handw. d. Chem. vi. 503).

**PICROCYANIC ACID.** Syn. with ISOPURPURIC ACID (iii. 433).

**PICROERYTHRIN.** $C^{12}H^{16}O^7$.—A body produced, together with orsellinic ether, by the action of boiling water on erythrin, in connection with which it has been already described (ii. 503).

*β-Picroerythrin*, $C^{13}H^6O^6$.—Lamparter (Ann. Ch. Pharm. cxxxiv. 243), by treating South American varieties of *Roccella fuciformis* with milk of lime, as in Stenhouse's process for the preparation of erythrin, has obtained a body which he calls *β-erythrin*, having the composition $C^{21}H^{24}O^{10}$; differing from that of erythrin by $CH^2$ (whence it might be called *methyl-erythrin*), resembling erythrin in most respects, but melting at 115°—116°, with violent evolution of carbonic anhydride, whereas erythrin melts, according to Hesse, at 137°, and does not give off carbonic anhydride till heated above 200°.

β-erythrin, boiled with *water*, yields orsellinic acid and β-picroerythrin. The reaction, and that by which ordinary picroerythrin is produced from erythrin, are represented by the equations:

$$\underset{\text{Erythrin.}}{C^{20}H^{22}O^{10}} + H^2O = \underset{\text{Orsellinic acid.}}{C^8H^8O^4} + \underset{\text{Picroerythrin.}}{C^{12}H^{16}O^7}.$$

$$\underset{\beta\text{-erythrin.}}{C^{21}H^{24}O^{10}} = \underset{\text{Orsellinic acid.}}{C^8H^8O^4} + \underset{\beta\text{-picroerythrin.}}{C^{13}H^{16}O^6}.$$

β-erythrin, boiled with strong *alcohol*, is resolved into orsellinic ether and β-picroerythrin:

$$\underset{\beta\text{-erythrin.}}{C^{21}H^{24}O^{10}} + \underset{\text{Alcohol.}}{C^2H^6O} = \underset{\substack{\text{Orsellinic}\\\text{ether.}}}{C^8H^7(C^2H^5)O^4} + \underset{\substack{\beta\text{-picro-}\\\text{erythrin.}}}{C^{13}H^{16}O^6} + H^2O.$$

On distilling off the alcohol, a syrupy residue is left which solidifies on cooling. The solution of this mass in boiling water yields on cooling silvery laminæ of orsellinic ether, and the mother-liquor evaporated to a syrup, deposits β-picroerythrin in stellate groups of needles.

Beta-picroerythrin has a slight acid reaction, and gives a red colour with chloride of lime. It is very soluble in water and in alcohol, sparingly in ether. It dissolves also in ammonia, and the solution forms with basic acetate of lead a white precipitate, and with nitrate of silver a reddish precipitate, which deposits metallic silver when warmed. When boiled with baryta-water, it yields carbonate of barium and β-orcin.

**PICROFLUITE.** A mineral consisting of a silicate combined with fluor spar and water, occurring at Lupikko, near Pitkäranta, in Finland. It is white, with a tinge of green or blue, single-refracting, with an unctuous to dull lustre: hardness = 2 to 3; specific gravity = 2·74. It melts before the blowpipe with intumescence and spirting, dissolves completely in acids, and gives off, with sulphuric acid, a large quantity of fluoride of silicon. Analyses, *a* by A. and J. Galindo, *b* by Arppe, gave

|  | $SiO^2$ | F | Ca''O | Mg''O | Fe''O | Mn''O | $H^2O$ |  |  |
|---|---|---|---|---|---|---|---|---|---|
| *a.* | 20·90 | 11·16 | 22·72 | 28·79 | 1·54 | 0·78 | 8·97 | = | 94·86 |
| *b.* | 32·16 | . . | 19·86 | 25·19 | 3·50 | . . | 9·08 |  |  |

These analyses lead to the formula $(4M''O.3SiO^2).2Ca''F^2.3H^2O$. (Arppe, Jahresb. 1862, p. 752.)

**PICROGLYCION.** *Dulcamarin.*—A substance contained, together with solanine and other matters, in bittersweet or *Stipites Dulcamaræ*, the stems of *Solanum Dulcamara.* It is obtained free from solanine by exhausting the aqueous extract of the stems with alcohol, distilling off the alcohol, dissolving the residue in water, precipitating the solution with basic acetate of lead, decomposing the lead-precipitate with sulphydric acid, and evaporating the filtrate to dryness. On treating the residue with acetic ether, and leaving the ether to evaporate, picroglycion is obtained in small stellate crystals, which may be freed from mother-liquor by pressure between paper.

Picroglycion has a sweet and bitter taste, melts very easily, and is decomposed, with carbonisation, at a higher temperature. It is very soluble in water, alcohol, and acetic ether; insoluble in common ether. It is not precipitated from its solutions either by metallic salts or by tincture of galls.

**PICROLICHENIN.** A substance contained, according to Alms (Ann. Ch. Pharm. i. 61) in *Variolaria amara.* It is extracted by alcohol, crystallised by evaporating the solution to a syrup, and purified by washing with a weak solution of potassic carbonate, and recrystallising from alcohol.

It forms truncated rhombic octahedrons, colourless, permanent in the air, inodorous, very bitter, and having a specific gravity = 1·176. It melts at 100°, and carbonises at a higher temperature, giving off vapours free from ammonia. It is insoluble in cold water, slightly soluble in boiling water, very soluble in alcohol, ether, volatile oils, and sulphide of carbon, and with aid of heat in fixed oils. The alcoholic solution has an acid reaction.

Picrolichenin is decomposed by nitric, hydrochloric, and phosphoric acid. With caustic *potash* it forms a red solution, from which acids precipitate a brown-red bitter substance. When left in contact with *ammonia* in a close vessel, it first becomes viscous and resinous, and ultimately dissolves, forming a liquid which is colourless at first, then turns reddish, finally saffron-yellow, and deposits after a while, shining yellow tufts of flattened tasteless needles easily soluble in alcohol and in caustic alkalis. They effloresce in dry air, give off ammonia when heated, and melt at 40° to a glutinous mass, having a deep cherry-red colour, and behaving with solvents like the crystals. The same red body is formed when the ammoniacal solution of picrolichenin is left to evaporate in the air. Its formation seems to show that picrolichenin is a source of orcin, and probably identical with one of the colouring acids of the lichens (lecanoric acid, &c.).

**PICROLITE.** A fibrous dark-green variety of serpentine, somewhat resembling asbestos; found in Silesia, and at Philipstadt in Wermeland, Sweden.

**PICROMERITE.** Potassio-magnesic sulphate, $K^2Mg''(SO^4)^2.6H^2O$, crystallised from the solutions of saline crusts, from the fumaroles of Vesuvian lavas of the eruption of 1855. (Scacchi.)

**PICROPHARMACOLITE.** See PHARMACOLITE (p. 387).

**PICROPHYLL** (from πικρός, bitter, and φύλλον, a leaf). A massive foliated, fibrous, magnesio-ferrous silicate, from Sala in Sweden. It has a deep greenish-grey colour; hardness = 2·5; specific gravity = 2·75. Before the blowpipe it turns black and then white, without melting; when moistened with cobalt-solution and ignited, it turns pale red. Contains 49·80 per cent. silica, 30 10 magnesia, 6·86 ferrous oxide, with trace of manganous oxide, 0·78 lime, 1·11 alumina, and 9·83 water (= 98·48), whence the formula $3(\frac{4}{5}Mg''.\frac{1}{5}Fe'')SiO^3.2H^2O$. It is perhaps an altered augite. (Svanberg, Pogg. Ann. l. 662.)

**PICROSMINE** (from πικρός, and ὀσμή, odour). A hydrated silicate of magnesium, occurring, with magnetic iron ore, near Presnitz, in Bohemia, in trimetric crystals, exhibiting the combination $\infty P \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, \breve{P}\infty$. Angle $\infty P : \infty P = 126° 52'$; $\infty\bar{P}\infty : \infty P = 153° 26'$; $\infty\breve{P}\infty : \breve{P}\infty = 121° 6'$; $\breve{P}\infty : \breve{P}\infty$ (over $\infty\breve{P}\infty$) = 62° 11'; adjacent = 117° 49'. Cleavage parallel to $\infty\breve{P}\infty$ perfect; parallel to $\infty\bar{P}\infty$, less so; traces parallel to $\bar{P}\infty$. It occurs also fine-columnar and granular. Hardness = 2 5—3. Specific gravity = 2·59—2·68. Lustre on cleavage-face pearly; elsewhere vitreous. Colour greenish-white, also dark green and grey. Streak white. Subtranslucent to opaque. Emits a bitter argillaceous odour when moistened. When heated it gives off water containing ammonia; behaves before the blowpipe like picrophyll. Contains 54·89 per cent. silica, 34·35 magnesia, 0·79 alumina, 1·40 ferric oxide, 0·42 manganous oxide, and 7·30 water (= 99·15), whence the formula $2Mg''SiO^3.H^2O$, the magnesium being partly replaced by iron. (Magnus, Pogg. Ann. vi. 53.)

**PICROTHOMSONITE.** A white radiate mineral, from the gabbro of Tuscany, containing, according to Bechi (Sill. Am. J. [2] xiv. 63), 40·35 per cent. silica, 31·25 alumina, 10·99 lime, 6·26 magnesia, 0·28 alkali, and 10·79 water. It is probably a thomsonite having the soda replaced by magnesia. (See THOMSONITE.)

**PICROTOXIC ACID.** The name given by Pelletier and Couerbe to picrotoxin, because it unites with metallic oxides.

**PICROTOXIN.** $C^{12}H^{14}O^5$. (Boullay, Ann. Chim. xxx. 209.—Casaseca, Ann. Ch. Phys. [2] xxx. 307.—C. Oppermann, Mag. Pharm. xxxv. 233.—Pelletier and Couerbe, Ann. Ch. Phys. [2] liv. 181.—Liebig, Ann. Ch. Pharm. x. 203.—Regnault, Ann. Ch. Phys. [2] lxviii. 160.—L. Barth, J. pr. Chem. xci. 155; Bull. Soc. Chim. 1864, ii. 388.)—The poisonous principle of the seeds of Cocculus indicus (*Menispermum Cocculus*). To prepare it, the pulverised seed is twice exhausted with boiling alcohol; the alcohol distilled off; the residual fat boiled out with a large quantity of water; and the brown aqueous extract mixed with a small quantity of neutral lead-acetate to remove colouring matter. The filtrate, freed from lead by sulphydric acid, is then evaporated, and the picrotoxin which separates is repeatedly crystallised from water till it becomes colourless.[*] (Barth.)

Picrotoxin usually crystallises from pure solutions in stellate groups of needles; from coloured liquids in interlaced spongy threads, which after a while change into more solid needles, more rarely into laminæ (probably containing water of crystallisation). It is permanent in the air, inodorous, has an intensely bitter taste, and is neutral to vegetable colours. It decomposes without fusion when strongly heated. It dissolves in 150 pts. of cold, and 25 pts. of boiling water; in 3 pts. of boiling alcohol of specific gravity 0·800; also in ether and in warm fixed oils. Its alcoholic solution turns the plane of polarisation to the left; $[\alpha] = -28°$ (Bouchardat and Boudet); $= -38°$ (Pfanndler) for a column 1 metre in length. It is very poisonous, producing vertigo, convulsions, and death.

*Analyses of Picrotoxin.*

| | Pelletier and Couerbe. | Oppermann. | | Regnault. | | Calculation $C^{12}H^{14}O^5$ |
|---|---|---|---|---|---|---|
| Carbon . . | 60·91 | 61·43 | 61·53 | 60·21 | 60·47 | 60·48 |
| Hydrogen . . | 6·00 | 6·11 | 6·22 | 5·83 | 5·70 | 5·88 |
| Oxygen . . | . . | . . | . . | . . | . . | 33·64 |
| | | | | | | 100·00 |

Oppermann, whose analyses differ considerably from all the rest, proposed the formula $C^5H^6O^2$, requiring 61·2 carbon and 6·1 hydrogen; but all the other analyses agree very nearly with the formula $C^{12}H^{14}O^5$. Barth's analyses also give 60·2 per cent. as the maximum percentage of carbon.

Picrotoxin unites with alkalis, baryta, lime, and oxide of lead, forming uncrystallisable compounds which are difficult to purify. On boiling it for some hours with dilute sulphuric acid, saturating with *carbonate of barium*, and evaporating the filtrate, there remains a syrup which dissolves in alcohol and dries up to a gummy mass having the composition $C^{24}H^{38}Ba''O^{16}$ or $C^{24}H^{26}Ba''O^{10}.6H^2O$. By boiling for 30 hours with dilute sulphuric acid and proceeding as above, a barium-compound is formed containing $C^{24}H^{34}Ba''O^{16}$ or $C^{24}H^{26}Ba''O^{10}.4H^2O$. The organic substance separated from this compound dissolves easily in water and alcohol, and dries up to a light yellow gummy mass, which when dried at 130°, has the composition $C^{24}H^{32}O^{12}$ or $C^{12}H^{16}O^6 = C^{12}H^{14}O^5.H^2O$.

Picrotoxin in many of its reactions exhibits the characters of a saccharine substance. It reduces *cupric oxide* from alkaline solutions, and when boiled with dilute acids, takes up water, forming a substance which also reduces cupric oxide. The reducing power of picrotoxin is, however, about five times less than that of glucose. With *nitric acid*, it yields oxalic acid, and when distilled with *soda-lime*, it gives off a small quantity of liquid having the odour of metacetone.

Picrotoxin dissolves in strong *sulphuric acid*, forming a saffron-coloured solution. With *sulphuric acid* and *potassic dichromate* it assumes a red-brown, and on heating a dark brown colour. (Schmidt.)

*Bromopicrotoxin*, $C^{12}H^{13}BrO^5$, is formed, with evolution of hydrobromic acid, by the action of bromine on picrotoxin. It separates slowly from alcoholic solution in soft crystalline groups, but on adding water to the solution, it is obtained as an amorphous flocculent precipitate, which dries up to a strongly electric powder.

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[*] During the recrystallisation of picrotoxin, there separates a small quantity of another substance (perhaps Boullay's menispermic acid, iii. 879), sparingly soluble in water, alcohol, and ether, but easily soluble in dilute sodic carbonate, and separated therefrom by acids in microscopic needles. Its analysis leads to the formula $C^9H^{12}O^5$

*Nitropicrotoxin*, $C^{12}H^{13}(NO^2)O^5$, is formed by dissolving picrotoxin in a mixture of strong nitric and sulphuric acid, and is precipitated by water as a flocculent mass which crystallises from dilute alcohol in small needles. It is not explosive, but decomposes when heated to 100°, or when the solution is boiled.

Detection of Picrotoxin.—The intensely bitter taste of picrotoxin has led to the use of cocculus grains as a substitute for hops in beer; and as it is a very poisonous substance, its detection in beer and other organic liquids becomes a matter of importance. For this purpose, T. J. Herapath absorbs the picrotoxin by means of animal charcoal, then dissolves it out by alcohol, and leaves it to crystallise from the alcoholic solution (see Beer, i. 537). According to W. Schmidt, however (J. pr. Chem. lxxxvii. 344; Jahresb. 1862, p. 629), this method cannot be depended upon for the detection of small quantities of picrotoxin, on account of the very slight absorbability of that substance by charcoal; the charcoal indeed appears to be useful rather for removing the colouring matter, resin, and extractive matter of the liquid, than for taking up the picrotoxin. The process recommended by Schmidt for the detection of picrotoxin in watery liquids such as beer, is as follows: The liquid is evaporated over the water-bath to a syrup; the residue is dissolved in a sufficient quantity of water to form a mobile liquid; this solution is agitated with 5 or 6 grms. of animal charcoal, and filtered after several hours; and the filtrate is completely precipitated with basic acetate of lead. The wine-yellow liquid separated from the precipitate is then repeatedly shaken up with 5 to 10 per cent. of amylic alcohol, and the oily layer, which contains the greater part of the picrotoxin, is decanted after standing for 24 hours. The portion of picrotoxin still remaining in the watery liquid may be separated by a repetition of this treatment. The united extracts are then left to evaporate in a moderately warm place; the yellowish residue is dissolved in weak spirit; the liquid evaporated to dryness; the residue boiled with water mixed with a small quantity of sulphuric acid; and the liquid is decolorised with animal charcoal, filtered, and evaporated till it acquires a distinctly bitter taste. It is then repeatedly shaken with ether, and the ethereal extract, after addition of a little alcohol, is left to evaporate. By repeatedly dissolving the residue in weak spirit, and leaving the solution to evaporate, the picrotoxin may be obtained in tufts of fine silky crystals. The charcoal used for decoloration and the lead-precipitates retain traces of picrotoxin, which may be dissolved out by hot alcohol. When picrotoxin is to be searched for in an alcoholic liquid, it is sufficient to evaporate, exhaust the residue with boiling water, decolorise the liquid with animal charcoal, concentrate the solution, and treat it with ether, &c., as above. J. W. Langley (Sill. Am. J. [2] xxxiv. 109) acidulates the suspected liquid, and agitates it with ether which takes up the picrotoxin, which may then be crystallised by evaporation on a watch-glass. According to Schmidt, on the other hand, picrotoxin does not crystallise from ether or from amylic alcohol.

The picrotoxin having been separated as above, is easily recognised by the great facility with which it crystallises from alcohol, and the peculiar characters of the crystals (i. 537); also by its strong bitter taste, its reaction with sulphuric acid and potassic chromate, and its power of reducing cupric oxide in alkaline solution.

**PICRYL** or *Cripin*. A substance formed, together with others, by submitting to dry distillation the crude product of the action of sulphydrate of ammonium on bitter-almond oil. On treating the distillate with ether, picryl dissolves together with stilbene, and separates after the latter, in colourless, inodorous, monoclinic octahedrons, insoluble in water, very soluble in ether, much less soluble in alcohol. It is attacked by chlorine, bromine, and nitric acid, yielding peculiar products. (Laurent.)

The name picryl is also used as synonymous with trinitrophenyl, $C^6H^2(NO^2)^3$, the radicle of picric acid, &c. *Chloride of Picryl* $C^6H^2(NO^2)^3Cl$ is obtained by the action of pentachloride of phosphorus on picric acid (p. 403). It is a yellow solid having an agreeable odour, soluble in alcohol and ether, not volatile without decomposition. Water decomposes it, yielding hydrochloric and picric acids; ammonia converts it into picramide.

**PICTITE.** Syn. with Sphene.

**PIDDINGTONITE.** A mineral constituting the principal part of a meteorite which fell on November 30, 1850, near Shalka in Bangoorah (East Indies), and was first described by Piddington (Journ. of the Asiatic Soc. of Bengal. 1852. xx. 299). The mineral consists, according to Haidinger (Wien. Akad. Ber. xli. 251; Jahresb. 1860, p. 848), of dark ash-grey, coarse-grained particles of rhombic or monoclinic structure, aggregated into spherical masses several inches in diameter, which are enclosed in a somewhat lighter, pumice-like mineral having a more fine-grained structure. The dark grey crystalline particles (piddingtonite) are composed of 57·66 per cent. silica, 20·65 ferrous oxide, 1·53 lime, 12·00 magnesia, with trace of alumina (= 98·84). The ash-grey mass encloses also small black granules of chrome-iron. The crust of the meteorite is very thin, of blackish-brown colour, with very little lustre.

**PIGOTITE.** An incrustation occurring on the granite cliffs of Cornwall, consisting of alumina combined with an organic substance called *mudesous acid* (iii. 1060).

**PIHLITE.** A doubtful mineral species between talc and mica, found at Fahlun in Sweden.

**PIMARIC ACID.** $C^{20}H^{30}O^2$. (Laurent, Ann. Ch. Phys. [2] lxxii. 384; [3] xxii. 459.—Sievert, Zeitschrift für die gesammten Naturwissenschaften, xiv. 311.)—An acid resin occurring in the turpentine of *Pinus maritima*, which hardens on exposure to the air, forming the substance called galipot; also in the colophony of Bordeaux (i. 1087). To prepare it, the galipot of commerce, after being freed from admixed turpentine, is pulverised and stirred up with a mixture of 1 pt. ether and 6 pts. alcohol, which is poured off after a short time. The undissolved portion treated twice more in the same way, and then dissolved in boiling alcohol, yields, after several days' standing, crystalline crusts, which must be promptly taken out and purified by recrystallisation from boiling alcohol (Laurent). It may also be obtained by washing Bordeaux colophony with cold alcohol, dissolving the residue in boiling alcohol, and leaving the solution to crystallise.

Pimaric acid forms white, warty, crystalline crusts, consisting of microscopic rectangular or sometimes six-sided prisms (Laurent); fine thin laminæ, the primary form of which is a quadratic prism often truncated on the edges, or acuminated (Sievert). It melts at about 125°, and solidifies only at 68°, to a limpid, sometimes crystallogranular mass; the acid dried in a vacuum loses under these circumstances 0·4 per cent. water (Laurent). It sinters together between 120° and 135°, and melts completely at 158° to a clear liquid from which the unaltered acid sublimes at 120°. In a capillary tube, both the crystallised and the already fused acid melt at 153° (Sievert). Specific gravity = 1·1047 at 18°. It is lævorotatory, but in a less degree than sylvic acid. It gives by analysis 78·18 per cent. carbon and 9·74 hydrogen (Laurent); 79·02 carbon and 9·87 hydrogen (Sievert), the formula $C^{20}H^{30}O^2$ requiring 79·47 carbon, 9·94 hydrogen and 10·59 oxygen. According to these results pimaric acid is isomeric with sylvic, and probably also with abietic acid.

Pimaric acid is insoluble in *water*, but dissolves in 10 pts. *alcohol* at 18° and in its own weight of boiling alcohol (Laurent); in 13 pts. alcohol of 92 per cent., in 2 pts. at the boiling heat (Sievert). Fused pimaric acid dissolves quickly when triturated with an equal weight of cold alcohol, but the solution solidifies almost immediately from separation of crystals.

*Amorphous Pimaric Acid.*—Crystallised pimaric acid becomes amorphous by keeping. It then dissolves in its own weight of alcohol, the solution not solidifying in the crystalline form, but depositing, when mixed with water, a soft mass having the same composition as crystallised pimaric acid. Pimaric acid in the fused state or dissolved in alcohol does not undergo this transformation (Laurent). Laurent subsequently regarded amorphous pimaric acid as identical with pinic acid.

The pimarates of the *alkali-metals* are soluble. The alcoholic solution of the acid does not precipitate the alcoholic solutions of the chlorides of *strontium*, *calcium* and *magnesium*, except on addition of ammonia, which produces a copious precipitate in the calcic solution, less abundant in the others. The alcoholic acid mixed at the boiling heat with the alcoholic solutions of *plumbic*, *cupric*, or *argentic acetate* forms amorphous precipitates after some time. The *lead-salt* dried in a vacuum contains 26·5 per cent. lead-oxide, agreeing approximately with the formula $C^{40}H^{58}Pb''O^4$, which requires 27·55 per cent

Pimaric acid distilled in a vacuum in quantities not exceeding 10 grms. yields first traces of water, then pyromaric acid solidifying for the most part in the neck of the retort, and ultimately leaves only a trace of charcoal. Larger quanties of the acid distilled in vessels containing air yield chiefly pimarone. Pimaric acid gradually added to strong *sulphuric acid* forms a brown-red solution, which if poured into water afters 24 hours deposits reddish-grey flocks.

By boiling with *nitric acid*, pimaric acid is gradually converted into nitromaric or azomaric acid, $C^{20}H^{28}(NO^2)^2O^4$, which collects on the surface of the liquid as a yellow friable resinous mass which may be purified by repeated boiling with water, or by solution in acid and precipitation with water. This acid decomposes when melted, leaving a bulky charcoal, but does not glow or deflagrate even when quickly heated. It burns like a resin, and yields by dry distillation a very small quantity of oil. It is insoluble in water, soluble in oil of vitriol, alcohol and ether; the alcoholic solution reddens litmus. It forms reddish-yellow salts, those of the *alkali-metals* being soluble, the *barium-salt* insoluble. The alcoholic solution of the acid forms yellowish precipitates with *neutral acetate of lead* and *nitrate of silver*.

**PIMARONE.** $C^{20}H^{30}O$.—When a considerable quantity of pimaric acid is distilled in a vessel containing air, and the viscid distillate, consisting of pimarone mixed with pyromaric acid, is saponified with potash, the pimarone is taken up into the soap formed by the pyromaric acid; and on agitating the pulverised soap with ether, the pimarone dissolves, together with a small quantity of potassium-salts, which may be removed by water. The residual pimarone, after being washed with dilute potash-ley and with water, and dried in a vacuum, is yellowish, has the consistence of a fixed oil, and dissolves in alcohol and ether. It hardens almost completely on exposure to the air.

**PIMELIC ACID.** $C^7H^{12}O^4 = \left.\begin{matrix}(C^7H^{10}O^2)''\\ H^2\end{matrix}\right\}O^2$. (Laurent, Ann. Ch. Phys. [2] lxvi. 163.—Bromeis, Ann. Ch. Pharm. xxxv. 104.—Gerhardt, Rev. scient. xix. 12.—Sace, Ann. Ch. Pharm. li. 221.—Arppe, *ibid.* cxv. 143; cxxiv. 98.—Gm. xii. 463.) This acid was discovered by Laurent in the mother-liquors resulting from the action of nitric acid on oleic acid, and is likewise produced by the action of nitric acid on wax, spermacetic and other fatty bodies. Sace obtained it by the action of nitric acid on linseed oil.

Laurent prepares it by boiling 200 or 300 grms. of oleic acid for twelve hours with an equal weight of nitric acid, cohobating the distillate from time to time. The nitric acid is then decanted, the undissolved portion again treated with a quantity of nitric acid equal to the former, and the ebullition continued for another twelve hours. This operation is repeated six or seven times till only about a fifth of the oleic acid remains undissolved. The decanted portions of nitric acid are then united and evaporated down to one-fourth. The residue left to itself for twelve hours deposits granules of suberic acid, which are to be pressed, moistened with cold water, again submitted to pressure, and the expressed liquids evaporated, the vessel being cooled from time to time, and the suberic acid which separates removed. This acid may be recognised by forming granules which are soft after being pressed with a glass rod. Gradually, however, pimelic acid begins to separate in hard sandy grains, mixed at first with suberic acid, which is easily removed by levigation with water. By a new evaporation more pimelic acid is obtained, but it crystallises very slowly, the deposition not being complete for several days. The evaporation must not be pushed too far, because the mother-liquor contains other acids of still greater solubility. The pimelic acid may be freed from adhering suberic acid by means of alcohol, which easily dissolves the latter, and finally purified by crystallisation from boiling water.

Pimelic acid forms grains of about the size of pins' heads, appearing under a magnifying glass as groups of crystals, the form of which cannot be made out. It is inodorous, but has an acid taste. It melts at about 114° (Laurent); at 134° (Bromeis); distils at a high temperature. 1 pt. of the acid dissolves in 35 pts. water at 18°; it is very soluble in boiling water, also in warm alcohol and ether; it dissolves also in hot strong *sulphuric acid*. When heated with *hydrate of potassium* it gives off hydrogen without blackening. The residue contains oxalic acid, and when treated with mineral acids gives off a volatile acid resembling valerianic acid (Gerhardt):

$$C^7H^{12}O^4 + 2H^2O = C^7H^2O^4 + C^5H^{10}O^2 + 2H^2.$$

Pimelic acid is dibasic, but only the neutral salts, $C^7H^8M^2O^4$ and $C^7H^8M''O^4$, are known.—The *ammonium-salt* gives off ammonia when boiled, and gradually on exposure. The acid neutralised with ammonia does not precipitate the salts of barium, strontium, calcium, magnesium, manganese or zinc. With *lead-salts* it forms a white precipitate, apparently insoluble in water and in alcohol; with *ferric salts*, a light-red precipitate; with *mercuric chloride*, a white precipitate.—The *copper-salt*, $C^7H^{10}Cu''O^4$, is a blue precipitate, insoluble in water and in alcohol.—The *silver-salt*, $C^7H^8Ag^2O^4$, is likewise obtained by precipitation.

**PIMELIC ETHERS.** *Pimelate of methyl*, $C^7H^{10}(CH^3)^2O^4$, is prepared like the ethyl-compound and decomposes in like manner when boiled.

*Pimelate of Ethyl*, $C^{11}H^{20}O^2 = C^7H^{10}(C^2H^5)^2O^4$, is obtained by the repeated action of hydrochloric acid on an alcoholic solution of pimelic acid. The portion which is volatile below 100° is distilled off, the residue neutralised with carbonate of sodium, and the dark red oil thereby separated, which increases in quantity on further addition of water, is dehydrated with chloride of calcium. The liquid thus obtained has a fruity odour, and gives by analysis 61·44 per cent. C and 9·76 H (calc. 61·11 C and 8·25 H). It begins to boil at 185°, but the boiling point gradually rises, charcoal separates, and a liquid passes over which effervesces with carbonate of sodium, and appears to be *ethyl-pimelic acid*, $C^7H^{11}(C^2H^5)O^4$. It gave by analysis 57·03 per cent. C and 9·10 H (calc. 57·44 per cent. C and 8·50 H). (Marsh, Ann. Ch. Pharm. civ. 125.)

*Pimelate of Amyl*, $C^{17}H^{32}O^4 = C^7H^{10}(C^5H^{11})^2O^4$.—Prepared like the preceding compound. Dark-red, somewhat oily liquid having a penetrating but not unpleasant odour. Boils between 170° and 200°. Insoluble in water, soluble in alcohol and ether (anal. 67·64 C and 10·99 H; calc. 68·00 C and 10·67 H). (Marsh, *loc. cit.*)

**PIMELITE.** A name applied to several green nickeliferous silicates:—*a.* Green chrysoprase earth, accompanying chrysoprase in Silesia (Klaproth, *Beiträge*, ii. 134). —*b.* Glocker's *Alizite*, a massive green mineral from Silesia, meagre to the touch, of specific gravity 1·458. Gives off water when heated; is infusible before the blowpipe; yields metallic nickel by reduction with sodic carbonate (C. Schmidt, Pogg. Ann. lxi. 388).—*c.* A similar mineral, but greasy to the touch, and of specific gravity 2·71—2·76. Behaves before the blowpipe like talc, and gives the reactions of nickel. Decomposed by acids both before and after ignition (Baer, J. pr. Chem. lv. 49):

| | $SiO^2$ | $Al^2O^3$ | $Fe^2O^3$ | $Fe''O$ | $Ni''O$ | $Mg''O$ | $Ca''O$ | $H^2O$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *a.* | 35·00 | 5·00 | 4·58 | . . | 15·63 | 1·25 | 0·42 | 38·12 | = | 100 |
| *b.* | 54·63 | 0·30 | . . | 1·13 | 32·66 | 5·89 | 0·16 | 5·23 | = | 100 |
| *c.* | 35·80 | 23·04 | 2·69 | . . | 2·78 | 14·66 | . . | 21·03 | = | 100 |

The first of these minerals, if the iron be supposed to exist as ferrous oxide and the alumina be reckoned with the acid, may perhaps be represented by the formula $(Ni''O ; Fe''O ; Mg''O).2SiO^2.7H^2O$. The second has the composition $\left.\begin{matrix}{}^3Ni''O\\ {}^4Mg''O\end{matrix}\right\}^2.3SiO^2.H^2O$. The third may be represented by the formula $3[(Mg''O ; Ni''O)^2SiO^2].2(2R^2O^3.3SiO^2).18H^2O$. This mineral contains organic remains, containing 0·44 per cent. carbon (according to Bayer). It loses 8·8 per cent. water at 110°, and 21·37 per cent. at a red heat.

**PIMENTO, OIL OF.** A volatile oil obtained from the fruit of *Myrtus Pimenta*, the pods of which yield 10 per cent. and the seeds 5 per cent. oil (Bonastre, J. Pharm. xi. 187). The crude oil is viscous, has a pale yellow or light brown colour, and strong refracting power; specific gravity = 1·03 at 8°. It resembles oil of cloves in taste and smell, and reacts like that oil with *sulphuric acid*, *nitric acid*, and *iodine;* dissolves completely in *alcohol* and *ether*.

By treatment with strong *potash-lye*, it is resolved into eugenic acid, $C^{10}H^{12}O^2$ (ii. 604), and a hydrocarbon polymeric with oil of turpentine, probably $C^{15}H^{24}$. This hydrocarbon is a colourless rather viscid oil, smelling somewhat like oil of turpentine, and exhibiting feeble lævo-rotatory power. Specific gravity 0·98 at 18°. Boiling-point 2·55. (C. Oeser, Ann. Ch. Pharm. cxxxi. 277; Bull. Soc. Chim. 1865, i. 434.)

**PIMPINELLA, OIL OF.** The volatile oil obtained by distilling the root of *Pimpinella saxifraga* with water, has a golden-yellow colour, a viscid consistence, a bitter, irritating taste, and is resinised by strong acids. The oil obtained in like manner from *Pimpinella nigra*, a variety of *P. saxifraga*, is light-blue and viscid (Bley, Trommsdorff, N. J. xii. [2] 29). Oil of anise (i. 297) is obtained from *Pimpinella anisum.*

**PINACOLIN.** $C^6H^{12}O$. (Fittig, Ann. Ch. Pharm. cxiv. 54.)—An oily body produced by the dehydration of pinacone, either by distilling the crystallised hydrate of pinacone with sulphuric or hydrochloric acid, or by subjecting fused pinacone to the action of dry chlorine gas. It is colourless, has an odour of peppermint, a specific gravity of 0·7999 at 16°, and boils at 105°. It is insoluble in *water*, but mixes in all proportions with *alcohol* and *ether*. It does not unite with acid sulphites of alkali-metal. With strong *nitric acid* it yields red-brown oily nitro-compounds. When subjected to the action of dry *chlorine* in diffused daylight, it is converted into dichloropinacolin, $C^6H^{10}Cl^2O$, which is a heavy viscid oil, solidifying after a while in colourless, needle-shaped crystals. It acts on the nose and eyes like dichloracetone (i. 30), melts at 51°, boils at 178°, is nearly insoluble in cold water, and sparingly soluble in hot water, from which however it crystallises. Its solution in ether or in absolute alcohol is precipitated by water.

**PINACONE.** $C^6H^{14}O^2$. (Fittig, Ann. Ch. Pharm. cx. 23; Jahresb. 1859, p. 342. —Städeler, Ann. Ch. Pharm. cxi. 277; Jahresb. 1859, p. 346.—Friedel, Ann. Ch. Pharm. cxxiv. 324; Jahresb. 1862, p. 404.—Linnemann, Ann. Ch. Pharm. Suppl.

iii. 374) —This body, isomeric with hexylene-glycol, $(C^6H^{12})''H^2O^2$, is produced by the action of sodium, or better of sodium-amalgam, on aqueous acetone:

$$2C^3H^6O \quad + \quad H^2 \quad = \quad C^6H^{14}O^2.$$

On distilling the resulting alkaline liquid, which also contains isotritylic alcohol, hydrate of pinacone, $C^6H^{14}O^2.6H^2O$, is found in the last portion of the distillate, and crystallises on cooling the liquid to a low temperature. This hydrate is resolved by further distillation into water and pinacone, which are easily separated by factional distillation, and from the first fraction, passing over between 170° and 180°, the pinacone may be obtained pure by repeated slow distillation. (Linnemann.)

Pinacone exists in two modifications, one liquid, the other solid. Liquid pinacone is a colourless syrup which has a specific gravity of 0·96 at 15°, does not solidify at 0°, boils at 176°—177° under a pressure of 0·738 met.; is soluble in water, but soon separates from the solution as a crystallised hydrate melting at 46·5°. If protected from moisture, it changes gradually but spontaneously into the solid modification.

Solid pinacone, when freed from the last traces of the liquid modification by pressure between paper, and purified by distillation, is a snow-white, finely crystalline mass, which gradually softens and melts between 35° and 38°, and boils at 171°—172° under a pressure of 0·739 met., giving off a colourless, inodorous, thickish liquid which soon solidifies. It dissolves readily in cold *alcohol* and *ether*, sparingly in cold *sulphide of carbon*, and crystallises from boiling sulphide of carbon in small needles. By spontaneous evaporation of an alcoholic or ethereal solution, it is obtained as a radio-crystalline mass made up of small needles. It is sparingly soluble in cold *water*, easily in hot water, but quickly separates from the solution as hydrated pinacone, melting at 46·5°. (Linnemann.)

Pinacone in either modification is easily reconverted into acetone by the action of acid *chromate of potassium* and *sulphuric acid*. (Linnemann.)

Hydrated pinacone, $C^6H^{14}O^2.6H^2O$ (regarded by Fittig and by Städeler as $C^6H^{12}O.7H^2O$). Obtained by the direct combination of pinacone with water, or in larger quantity by the action of sodium-amalgam on aqueous acetone (*vid. sup.*). It is a light transparent substance usually crystallising in thin four-sided tablets (hence the name, from πίναξ, a table), but sometimes, according to Städeler, in long prismatic crystals. When pure it is perfectly inodorous. When kept in close vessels it volatilises, and sublimes from one part of the vessel to another, even at ordinary temperatures. It is sparingly soluble in cold *water* and *ether*, easily soluble in *alcohol*, and may be recrystallised from hot water. It melts at 46·5° to a colourless liquid which solidifies on cooling. It is resolved by dry distillation into pinacone and water, but volatilises undecomposed with aqueous vapour (Linnemann). By distillation with sulphuric or hydrochloric acid, or by exposure in the melted state to the action of dry chlorine, it is converted into pinacolin. (Städeler.)

Fittig appears to have obtained two other hydrates of pinacone, viz. $C^6H^{14}O^2.2H^2O$ and $C^6H^4O^2.H^7O$.

**Benzopinacone.** $C^{26}H^{22}O^2$ (Linnemann, Ann. Ch. Pharm. cxxxiii. 26). This compound, related to benzone (phenyl-benzoyl, p. 478) in the same manner as pinacone to acetone, is produced by the action of zinc and dilute sulphuric acid on benzone:

$$2C^{13}H^{10}O \quad + \quad H^2 \quad = \quad C^{26}H^{22}O^2.$$

To prepare it, 1 pt. of an alcoholic solution of benzene saturated at 15°, is added to 6 pts. of a mixture of 1 pt. oil of vitriol, 1 pt. water and 4 pts. alcohol, and as much granulated zinc is added as can be just covered by the liquid. On leaving the mixture to itself for a few days, the benzopinacone is gradually deposited as a crust on the zinc, and that which still remains dissolved may be separated either by distilling off the alcohol or by precipitating with water. The portion attached to the zinc is easily loosened by treating the zinc with dilute sulphuric acid, and the whole may then be separated by levigation, and purified by repeated crystallisation from boiling alcohol.

Benzopinacone crystallises in microscopic, transparent, well-defined prisms, sparingly soluble in boiling *alcohol*, easily in *ether*, *chloroform* and *sulphide of carbon*. It melts between 170° and 180°, without solidifying again. By fusion and distillation it is converted into an isomeric modification.

Benzopinacone is intermediate in composition between benzone and benzhydrol (p. 478), and is converted into the former by oxidation with dilute *chromic acid:*

$$C^{26}H^{22}O^2 \quad + \quad O \quad = \quad 2C^{13}H^{10}O \quad + \quad H^2O;$$

and into the latter by the action of *sodium-amalgam* on its alcoholic solution:

$$C^{26}H^{22}O^2 \quad + \quad H^2 \quad = \quad 2C^{13}H^{12}O.$$

Benzopinacone boiled with excess of *chloride of benzoyl*, gives off hydrochloric acid,

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and is converted, by abstraction of 1 at. water, into a substance having the composition $C^{26}H^{20}O$, and related to benzopinacone in the same manner as pinacolin (p. 647) to pinacone. By treating the product with strong aqueous potash, exhausting the residual powder with ether, and recrystallising from boiling benzene, the compound $C^{26}H^{20}O$ is obtained as a white indistinctly crystalline powder, soluble in boiling alcohol, ether and benzene, and melting at 182°. It differs from benzhydrolic ether (p. 478) by only 2 at. hydrogen; nevertheless it is not converted into that body by treatment with sodium-amalgam.

*Isobenzopinacone.*—Benzopinacone is converted by fusion or distillation into a liquid which has the same composition, but does not solidify even at −15°. This modification of benzopinacone is a syrupy, strongly refracting liquid, which boils without decomposition at 297·5° under a pressure of 0·733 met., and has a specific gravity of 1·10 at 19°. By transmitting a cone of light through it in a darkened space, a blue fluorescence is produced. It dissolves easily in cold alcohol, ether and benzene. With chloride of benzoyl, it gives off hydrochloric acid, but forms a fluid, not a solid product.

*Solid Isobenzopinacone.*—When the liquid modification just described is left to itself for some months, it solidifies gradually but completely, forming a substance which dissolves easily in cold alcohol, ether and benzene, and melts at 31°, whereas the melting-point of ordinary benzopinacone is between 170° and 180°. It is converted with extraordinary facility into the fluid modification, remaining in the liquid form when its solutions are left to evaporate, and undergoing complete liquefaction when an attempt is made to pulverise it.

Both the liquid and the solid modification of isobenzopinacone, when treated with sodium-amalgam, are converted, like benzopinacone itself, into benzhydrol.

**PINCHBECK.** An alloy of copper and zinc, usually containing about 9 pts. copper to 1 pt. zinc. (See COPPER, ALLOYS OF, ii. 49.)

**PINE-OIL** or *Fir-oil.* These names are applied to certain oils resembling oil of turpentine, obtained in various ways from pine and fir-trees. An oil of this kind is extracted in the Black Forest from the seeds of *Pinus picea* and *Pinus abies.* It is limpid, of golden-yellow colour, very mobile, dries rapidly, and does not solidify till cooled to about −30°. It is used in the preparation of colours and varnishes (Gerhardt's *Traité*, ii. 901). A similar oil, formerly used in medicine, is prepared by distilling the young branches and needles of the dwarf pine (*Pinus Pumilio*) with water. It is mobile, has a faint yellowish colour and agreeable balsamic odour; a specific gravity of 0·893 at 17°; and boils at 152°. By rectification with water and dehydration over chloride of calcium, it is obtained colourless. Hydrate of potassium immersed in it becomes covered with a brown resinous substance. By repeated treatment with potassium and rectification in a stream of carbonic anhydride, it yields a hydrocarbon, $C^{10}H^{16}$, less fragrant than the original oil, having a specific gravity of 0·875 at 17°, boiling at 161°. This hydrocarbon is lævo-rotatory, a stratum 25 c. m. thick turning the plane of polarisation 18° to the left. It absorbs hydrochloric acid gas, forming a yellow liquid compound $C^{10}H^{16}.HCl$, of specific gravity 0·982 at 17°, and smelling somewhat like oil of thyme. (Mikolaech, Jahresb. 1860, p. 478.)

The following are the quantities of oil extracted by sulphide of carbon from the seeds of various species of *Pinus* (dried at 100°). The shelled seeds of *Pinus sylvestris* yield from 20·3 to 23·4 per cent. oil; of *P. Picea*, 7·8; unshelled seeds of *P. Cembra*, 29·2; shelled seeds of the same, 36·5; unshelled seeds of *P. Strobus*, 29·8; of *P. Abies*, 20·6; of *P. Larix*, 17·8; of *P. Pumilio*, 17·5; of *P. canadensis*, 11·4—12·9; of *P. maritima*, 22·5—25·0. All the seeds examined were several years old. (Wagner, Dingl. pol. J. clx. 466; Jahresb. 1860, p. 714.)

**PINE-RESINS.** *a. Resins of Turpentine.*—Turpentine, the resinous juice which exudes spontaneously, or from incisions in the stems of firs, pines, and other coniferous trees, is a mixture of a volatile oil ($C^{10}H^{16}$) with a resin called colophony, $C^{20}H^{30}O^2$ (i. 1087), probably formed by oxidation of the volatile oil:

$$2C^{10}H^{16} \quad + \quad O^3 \quad = \quad C^{20}H^{30}O^2 \quad + \quad H^2O.$$

This resin is chiefly a mixture of two isomeric acids, namely, sylvic acid, which is crystalline, and pinic acid, which is amorphous. The turpentine which exudes during the winter months from incisions made towards the end of autumn, solidifies round the edges of the incisions in opaque yellowish-white crusts, called gallipot, consisting of a mixture of essential oil of turpentine with another crystalline resinous acid, called pimaric acid (p. 644), likewise having the composition $C^{20}H^{30}O^2$. (See these several acids; also TURPENTINE.)

*β. Resins of Pinus sylvestris.*—The needles of the Scotch fir contain several resinous matters, which have been examined by Kawalier (Wien. Akad. Ber. xi. 344 xiii. 325).

1. *Kinovous acid*, $C^{12}H^{18}O^{2}$ [?].—To obtain this acid, the needles are cut up and boiled with alcohol of 40°; the alcoholic decoction is distilled in the water-bath, the greater part of the volatile oil then passing over with the alcohol; and the distillate is mixed with water. It is thereby separated into a dark green resinous mass containing ceropic acid (i. 836), kinovous acid, a small quantity of volatile oil, and a turbid watery liquid in which pinipicrin, sugar, traces of citric acid, oxypinitannic acid, and pinitannic acid remain dissolved. The needles exhausted with alcohol still contain a little pinipicrin and jelly. The resinous mass is dissolved in alcohol of 40°; an alcoholic solution of neutral acetate of lead is added, which throws down impure ceropate of lead; sulphydric acid gas is passed into the filtrate; and the precipitated mixture of chlorophyll and sulphide of lead is separated by filtration. The now yellow filtrate deposits, after the alcohol has been distilled off, a semi-fluid resin, which dissolves in very dilute potash-ley, to a light brown liquid, from which the *resins* may be precipitated, in combination with lime, by chloride of calcium. These resins are filtered off and washed with water, and the filtrate and wash-water are precipitated with a slight excess of hydrochloric acid, whereby faintly yellow flocks of kinovous acid are precipitated, to be purified by redissolving them in dilute potash, treating the solution with animal charcoal, and precipitating the filtrate with hydrochloric acid.

Kinovous acid is a white, or slightly yellow brittle mass, yielding a strongly electric powder. Its solution in lime-water yields, with nitrate of silver, a precipitate having, according to Kawalier, the composition $2C^{12}H^{18}O^{2}.5Ag^{2}O.H^{2}O$.

2. *Resin*, $C^{15}H^{40}O^{2}$.—The compound of resin and lime, precipitated by chloride of calcium in the preparation of kinovous acid, dissolves almost completely in ether; and if the solution be evaporated, the residue digested in alcohol of 40°, the solution again evaporated, and the residue treated with dilute hydrochloric acid, chloride of calcium dissolves, and a brownish-yellow resin is left, having the composition just mentioned. When distilled with hydrate of calcium, it yields two oils containing respectively $C^{30}H^{48}O$, and $C^{50}H^{80}O$, both of which, when twice distilled over phosphoric anhydride, are converted into an oily hydrocarbon, $C^{10}H^{16}$. The resin dropt in the fused state upon soda-lime heated to 220°, splits up into oily products comparatively rich and comparatively poor in oxygen (Kawalier). See *Gmelin's Handbook*, xv. 33.

**PINEY TALLOW** or *Malabar tallow*. A fat obtained by boiling the fruit of *Valeria indica*, a tiliaceous tree indigenous in Malabar. It is a whitish-yellow, waxy mass, having a faint agreeable odour, a density of 0·9625, melting at 37·5°, slightly soluble in cold alcohol. According to Marcet and Babington, it contains 77·0 per cent. carbon, 12·3 hydrogen and 10·7 oxygen. (*Gmelin's Handbook*, xvi. 400.)

**PINGUITE.** A mineral from Wolkenstein in Saxony, resembling chloropal (i. 921), but having a greasy feel and specific gravity 2·3—2·35. Contains, according to Kersten (Schw. J. lvi. 9), 36·90 silica, 1·80 alumina, 29·50 ferric oxide, 6·10 ferrous oxide, 0·4 manganous oxide, 0·45 magnesia and 25·11 water, which may be represented approximately by the formula $(2Fe''O.3SiO^{2}).4(\overset{\prime\prime\prime}{Fe}{}^{2}O^{3}.2SiO^{2}).30H^{2}O$.

*Gramenite* from Mengenberg in the Siebengebirge, has nearly the same composition, viz. 38·39 per cent. $SiO^{2}$, 6·87 $Al^{2}O^{3}$, 25·46 $Fe^{2}O^{3}$, 0·56 CaO, 0·67 MnO, 0·75 MgO and 23·36 water. (Bergemann.)

**PINIC ACID.** $C^{20}H^{30}O^{2}$. *Amorphous resin of colophony, Alpha-resin of turpentine.* (Berzelius.)—This acid, isomeric with sylvic and with pimaric acid, constitutes the principal portion of colophony and appears to be identical with amorphous pimaric acid (p. 644). To extract it from colophony, that substance is treated with cold alcohol of 72°, which dissolves it in preference to the crystallisable sylvic acid. The liquid precipitated by an alcoholic solution of cupric acetate, yields a salt whence the pinic acid may be separated by means of any mineral acid.

Pinic acid is an amorphous resin, exactly like colophony, insoluble in water, but soluble in alcohol, ether, and oils, both fixed and volatile. It melts when heated, and decomposes at a higher temperature. With the aid of heat it decomposes carbonates, and separates the fatty acids from the alcoholic solutions of their soaps. (Unverdorben, Pogg. Ann. xi. 27.)

**PINICORRETIN.** $C^{24}H^{38}O^{5}$[?]. (Kawalier, Wien. Akad. Ber. xi. 359.)—A substance occurring in the bark of the Scotch fir (*Pinus sylvestris*). The bark of the upper parts of the stem, after being freed from the outer rind, is cut in pieces, and boiled with alcohol of 40 per cent.; the ceropic acid which separates from the decoction on cooling is separated by filtration; the greater part of the alcohol is evaporated; the residual liquid is mixed with water; and the turbid solution is treated with neutral acetate of lead, whereby pinicortannic acid and pinicorretin are precipitated, while cortepinitannic acid (ii. 85) and sugar remain in solution. The washed lead-precipitate, digested with very dilute acetic acid, separates into pinicortannic acid (*infra*), which dissolves (and may be obtained by precipitating with basic acetate of lead, decomposing the precipitate with sulphydric acid, and evaporating the filtrate out of contact with air), and a dark-coloured glutinous residue, soluble in strong alcohol. On treating the solution with sulphydric acid, and evaporating the filtered liquid, pinicorretin remains behind, and may be purified by solution in alcohol.

Pinicorretin is a black-brown glutinous mass, very slightly soluble in ammonia. The ammoniacal solution yields, with chloride of barium, red-brown flocks containing $4Ba''O.3C^{24}H^{36}O^5$.

**PINICORTANNIC ACID.** $C^{32}H^{36}O^{21}$[?]. (Kawalier, Wien. Akad. Ber. xi. 360.)—An acid occurring in the bark of *Pinus sylvestris*, and obtained, as above, in the preparation of pinicorretin. It is also produced when the solution of cortepinitannic acid (ii. 85) is evaporated in contact with air. It is a red-brown powder, converted by boiling with water containing hydrochloric acid, into a bright red powder containing $3C^{16}H^{8}O^{10}.H^2O$. Its aqueous solution colours ferric chloride green.

**PINIPICRIN.** $C^{22}H^{36}O^{11}$. (Kawalier, Wien. Akad. Ber. xi. 350, xiii. 515.)—A bitter substance occurring in the needles, inner bark and outer bark of the Scotch fir (*Pinus sylvestris*), and in the green parts of *Thuja occidentalis*.

*Preparation.*—The comminuted needles of the Scotch fir (or branches of Thuja) are exhausted with alcohol of 40°; the alcohol is distilled off from the decoction; and the residue is mixed with water, which separates a green mass of resin (serving for the preparation of kinovous acid, p. 649), while the supernatant turbid liquid retains in solution pinipicrin, sugar, traces of citric acid, oxypinitannic acid, and pinitannic acid. This liquid is mixed with a few drops of neutral acetate of lead, which renders it filtrable; the filtrate is mixed with excess of that reagent, which throws down oxypinitannate of lead; then, after another filtration, pinitannate of lead is precipitated by the basic acetate; this is also separated by filtration after the liquid has cooled; and the filtrate is saturated with sulphydric acid. The liquid, freed from sulphide of lead and evaporated in a stream of carbonic acid, leaves a residue of the consistence of an extract, from which anhydrous ether-alcohol extracts the pinipicrin and leaves the sugar. A small quantity of foreign matter is precipitated from the solution by basic acetate of lead; the filtrate is treated with sulphydric acid; the sulphide of lead is removed, and the liquid evaporated. By repeatedly dissolving the residue left after the ether-alcohol has been distilled off, in fresh quantities of anhydrous alcohol containing ether, as long as any insoluble matter is left, and evaporating the solution, pinipicrin is at length obtained, still, however, contaminated with acetic acid, which adheres to it obstinately, but may be removed by agitation with a little pure ether (which, however, at the same time, removes a little pinipicrin). The needles, after exhaustion with alcohol, still retain a little pinipicrin, which may be obtained from the aqueous decoction in the same manner as from the alcoholic.

*Properties.*—Pinipicrin is a bright yellow powder, which softens at 55°, becomes viscid at 80°, transparent and mobile at 100°, and solidifies on cooling to a brownish-yellow, brittle, friable mass. It is hygroscopic, and has a strong bitter taste. It is very soluble in *water*, dissolves also in *alcohol*, *ether-alcohol*, and *aqueous ether*, but not in pure ether.

Pinipicrin swells up strongly when heated on platinum-foil, and leaves a difficultly combustible charcoal. The aqueous solution, when heated, instantly gives off the odour of ericinol (ii. 499), and is completely resolved into this substance and glucose:

$$C^{22}H^{36}O^{11} \quad + \quad 2H^2O \quad = \quad 2C^6H^{12}O^6 \quad + \quad C^{10}H^{16}O.$$

In contact with *emulsin*, it emits an odour of volatile oil, but the action soon ceases. (Kawalier, Wien. Akad. Ber. xii. 549.)

**PINITANNIC ACID.** $C^{14}H^{16}O^{8}$[?]. (Kawalier, Wien. Akad. Ber. xi. 357; xxix. 19.)—This acid occurs, together with thujin and thujigenin, in the green parts of the common *Arbor vitæ* (*Thuja occidentalis*), and is precipitated, partly from the aqueous extract, together with thujin, by neutral acetate of lead, partly, together with thujigenin, on subsequent addition of basic lead-acetate,—remaining in solution when these precipitates are decomposed by sulphydric acid, and the thujin and thujigenin have crystallised out. The mother-liquors are then evaporated to dryness; the pinitannic acid extracted by anhydrous ether-alcohol; the filtrate quickly evaporated to dryness over the water-bath; and the remaining acid dried in a vacuum over oil of vitriol.

Pinitannic acid occurs also, together with oxypinitannic acid (p. 319) and pinipicrin, in the needles of old Scotch fir trees, and is obtained as a lead-salt in the preparation of pinipicrin (*vid. sup.*), by precipitation with basic acetate of lead, after the oxypinitannic acid has been precipitated by the neutral acetate. The washed precipitate is decomposed by sulphydric acid, and the liquid is heated with the sulphide of lead, then filtered, and evaporated to dryness in a stream of carbonic anhydride.

Pinitannic acid is a yellow-red, or if prepared from Thuja, a brownish-yellow powder, having a slightly bitter astringent taste, becoming soft and glutinous at 100°. It dissolves readily in *water*, *alcohol*, and *ether*; does not precipitate solution of gelatin. The aqueous solution colours *ferric chloride* dark brown-red, forms yellow precipitates with *neutral* and *basic acetate of lead*, and precipitates *cupric sulphate* and *silver-nitrate*, the latter on addition of ammonia. When boiled with a small quantity of *stannic chloride*, it imparts a permanent yellow dye to woollen stuffs mordanted with alum or tin-salt.

**PINITE.** $C^6H^{12}O^5$. (Berthelot, Ann. Ch. Phys. [3] xlvi. 76; Chim. org. ii. 213.—Johnson, Sill. Am. J. [2] xxii. 6; Gm. xv. 212.)—A saccharine substance contained in the sap of the *Pinus Lambertiana* of California. It is deposited from the aqueous extract of the crude hardened juice, in hard white radio-crystalline nodules of specific gravity 1·52; as sweet as sugar-candy, very soluble in *water*, nearly insoluble in absolute *alcohol*. It is dextro-rotatory, not fermentable and does not reduce solution of *potassio-cupric tartrate*, even after treatment with sulphuric acid. It is decomposed by hot *nitric acid*, with formation of nitro-compounds and a small quantity of oxalic acid. With an ammoniacal solution of *lead-acetate*, it forms a precipitate containing $C^6H^{12}O^5.2Pb''O$. With *acids* it forms ethers analogous to the mannitanides and dulcitanides: thus with *benzoic acid* it forms dibenzopinite, $C^{20}H^{20}O^7 = C^6H^{12}O^5 + 2C^7H^6O^2 - 2H^2O$, and tetrabenzopinite $C^{34}H^{32}O^{11} = C^6H^{12}O^5 + 4C^7H^6O^2 - 2H^2O$; and analogous compounds with *stearic acid*. All these compounds are neutral. With *tartaric acid*, it forms pinitartaric acid, $C^{30}H^{36}O^{35} = C^6H^{12}O^5 + 6C^4H^6O^6 - 6H^2O$, which yields calcium-salt containing $C^{30}H^{30}\overset{''}{Ca}{}^3O^{35}.6H^2O$.

**PINITE** is also the name of a mineral formed from dichroïte (ii. 320) by the action of alkaline waters. It occurs in six- or twelve-sided prisms, with cleavage often indistinct, sometimes basal; colour grey to greyish-green or brown. Hardness = 2·5. Like other minerals formed by decomposition of dichroïte, it is not perfectly definite in composition, but exhibits various stages of transition between dichroïte and mica.

*Analyses: a.* From near Schneeberg in Saxony: blue-green mass covered with a micaceous crust (which was removed as completely as possible previously to the analysis) (Rammelsberg, *Mineralchemie*, p. 835).—*b.* From Penig in Saxony, similar to the preceding, but with a red crust rich in ferric oxide (Rammelsberg). *c.* From Stolpen in Saxony: so called *prismatic mica*; red (Massalin, Trommsd. N. J. iv. 2, 324).—*d.* From Saxony; specific gravity = 2·75 (Marignac, Bibl. univ. 1847, iv. 157).—*e.* From Auvergne; *α.* C. Gmelin (Kastn. Arch. i. 226); *β.* From St. Pardoux (Rammelsberg); *γ.* Specific gravity = 2·74 (Marignac).—*f.* From Mont Breven in the valley of Chamounix; specific gravity = 2·84 (Marignac).—*g.* From Diana, New York: green six-sided prisms of specific gravity 2·75; decomposible by acids (Brush, J. pr. Chem. lxxv. 453).

| | *a.* | *b.* | *c.* | *d.* | *e.* | | | *f.* | *g.* |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *α.* | *β.* | *γ.* | | |
| Silica | 46·38 | 47·00 | 45·0 | 46 10 | 55 96 | 48·92 | 47·50 | 44·70 | 45·55 |
| Alumina | 27·65 | 28 36 | 30·0 | 32·46 | 25·48 | 32·29 | 31·80 | 31·64 | 31·62 |
| Ferric oxide | 8·71 | 7·86 | 12·6 | 4 27 | 5·51 | 3·49 | 3·52 | 6 57 | 0 98 |
| Magnesia | 1 02 | 2 48 | . . | 2·26 | 3·76 | 1·41 | . . | 2·86 | 3 38 |
| Lime | 0·49 | 0·79 | . . | . . | . . | 0·31 | 0·92 | . . | 2 42 |
| Potash | 6·52 | 10·74 | 12·4 | 9·00 | 7·89 | 9 14 | 9·05 | 7·89 | 8 11 |
| Soda | 0·40 | 1·07 | . . | 0·46 | 0·38 | . . | 1·78 | 0 95 | 1·06 |
| Water | 7·80 | 3 83 | . . | 5·45 | 1·41 | 4 27 | 5·03 | 5·39 | 7 32 |
| | 99·42 | 102·13 | 100 0 | 100·00 | 100·39 | 100·03 | 100·00 | 100·00 | 100·44 |

**PINITOÏD.** This name is applied to certain minerals more or less resembling pinite in composition and physical characters.—*a.* Greyish-green or greenish-white nodules of crystallo-granular structure, specific gravity 2·7888, and hardness about 2 5, occurring in the felsite-tufa of the Zeisigwald near Chemnitz (A. Knop, Jahresb. 1859, p. 794).—*b.* Pseudomorphs after felspar occurring in decomposed porphyry, from the Klitzschmühle near Oberwiesa (after separation of the felspar-sand by levigation) (Knop).—*c.* A fine-splintery decomposition-product of oligoclase (hardness = 2·5), imbedded in the porphyritic granite of Sasbachwalden in the northern part of the Black Forest (F. Sandberger, Jahresb. 1861, p. 1008).—*d.* A mineral forming the substance of vegetable petrifactions in the phyllite of Petit-Cœur in the Tarantaise, Savoy (Terreil, Jahresb. 1861, p. 1008).—*e.* A light green or white substance of the consistence of kaolin, occurring in clefts of a slate imbedded in the spiriferous sandstone of Ems in Nassau (E. Herget, Jahresb. 1862, p. 822):

| | $SiO^2$. | $Al^2O^3$. | $Fe^2O^3$. | FeO. | MgO. | CaO. | $K^2O$. | $Na^2O$. | $H^2O$ | $P^2O^5$. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *a.* | 47·77 | 32·65 | . . | 8·94 | 0·49 | . . | 5·86 | 1·50 | 4·19 | | = | 101·40 |
| *b.* | 54·65 | 28·77 | . . | 4·32 | 1·12 | . . | 4·92 | | 6·22 | | = | 100 |
| *c.* | 50·43 | 28·89 | | . . | 3·48 | . . | 5·12 | 3·68 | 5·84 | | = | 97·44 |
| *d.* | 50·00 | 36·45 | 0·37 | . . | 0·45 | | 5·01 | . . | 7·96 | trace | = | 100·24 |
| *e.* | 53·15 | 33·56 | . . | . . | 0·17 | 0·21 | 4·70 | . . | 8·21 | | = | 100 |

**PINOLIN.** A volatile oil produced by the distillation of American pine-resin, and used as an illuminating material.

**PINUS.** The Stone Pine (*Pinus Picea*) growing in the south of Europe, yields large oblong oleaginous seeds (called *pignons* by the French) which are used as food; their nutritive power in the dry state is about equal to that of walnuts: but in the fresh state they are more nutritive than fresh walnuts. According to Payen (Bull. Soc. Chim. 1865, i. 235), they contain 5·71 per cent. water, 42·50 fat oil, 39·45 nitrogenous matter (nitrogen 6·44), 0·50 cellulose, and traces of starch, and 4·14 inorganic matter. The seeds exhausted of oil yield 11·87 per cent. nitrogen and 9·04 ash.

The ash of *Pinus Mughus* and *P. Pumilio*, and the soils on which they grow, have been analysed by H. S. Jobson (Ann. Ch. Pharm. xcv. 226; Jahresb. 1855, p. 709); the latter also by Wittstein (Jahresb. 1862, p. 511); the ash of *Pinus sylvestris* by Heyer and Vonhansen (Ann. Ch. Pharm. lxxxii. 180; Jahresb. 1852, p. 798).

Respecting the oils obtained from various kinds of pine, see page 648. For the various resins and other substances obtained from the bark and needles of *Pinus sylvestris*, see Kawalier (Wien. Akad. Ber. xi. 344; Ann. Ch. Pharm. lxxxviii. 360; Jahresb. 1853, p. 570; *Gmelin's Handbook*, xv. 33, 487; xvi 26); also the articles Ceropic Acid, Cortepinitannic Acid, Ericinol, Kinovous Acid, Oxypinitannic Acid, Phlobaphene, Pine-resins, Pinicorretin, Pinicortannic Acid, Pinipicrin, Pinitannic Acid, Tannecortipinic Acid, and Tannopic Acid, in this Dictionary.

**PIOTIC ACID.** Syn. with Metamaroaric Acid (iii. 976).

**PIOTOUS ACID.** Syn. with Hydromargaritic Acid (iii. 205).

**PIPER.** Black pepper (*Piper nigrum*) yields a volatile oil, having the composition of turpentine-oil, and boiling at 167·5°. Specific gravity of the oil = 0·864; of the vapour = 4·73. The oil absorbs a large quantity of hydrochloric acid, without forming a crystalline compound. (Souheiran and Capitaine, J. Pharm. 1840, p. 65.)

The root of *Piper methysticum*, or Kawa, has been already described under the latter name (iii. 445).

**PIPERIC ACID.** $C^{12}H^{10}O^4$. (Von Baho and Keller, *Dissertation von C. Keller*, Freiberg, 1856, p. 16.—Strecker, Ann. Ch. Pharm. cv. 317; cxviii. 280.—G. C. Foster, Chem. Soc. Qu. J. xv. 17.—Gm. xv. 7.)—An acid produced, together with piperidine, by boiling piperine with potash:

$$\underset{\text{Piperine.}}{C^{17}H^{19}NO^3} + H^2O = \underset{\text{Piperic acid.}}{C^{12}H^{10}O^4} + \underset{\text{Piperidine.}}{C^5H^{11}N.}$$

*Preparation.*—1 part of piperine is boiled with 3 pts. of potassium-hydrate and 16 to 20 pts. absolute alcohol, the liquid which distils over being continually poured back and the process continued for twelve hours, or till a sample of the mixture taken out of the retort is no longer precipitated by water (V. Babo and Keller); or better, equal weights of piperine and potassium-hydrate, with as much strong alcohol as is required to dissolve both, are heated for four or five hours to 100° in a closed vessel (Foster). The crystalline plates of potassic piperate which are thereby produced in abundance, are separated from the brown mother-liquor, purified by repeated crystallisation from a small quantity of boiling water, with help of animal charcoal; then dissolved in water and decomposed by dilute hydrochloric acid; and the acid, which separates as a jelly, is collected, washed, and purified by repeated crystallisation from alcohol. Another method is to neutralise the aqueous solution of the impure potassium-salt with acetic acid, mix it with a small quantity of solution of acetate of lead, separate the lead dissolved in the filtered liquid by sulphydric acid, filter again, and evaporate to the crystallising point. (V. Babo and Keller.)

*Properties.*—Piperic acid forms yellowish capillary needles; in the moist state, a sulphur-yellow jelly which shrinks on drying. Melts at 150°, sublimes at about 200°, partly unaltered, emitting an odour of coumarin, and leaving a brown fused residue. Its reaction is scarcely acid (V. Baho and Keller). It is nearly insoluble in *water*; dissolves in 270 pts. of cold absolute *alcohol*, easily in the same liquid at the boiling heat; sparingly in *ether*, scarcely at all in *sulphide of carbon* or *rock-oil*; somewhat more easily in *benzene*.

*Decompositions.*—1. Piperic acid burns when heated in contact with the air, emitting an odour of anise, and leaving a difficultly combustible charcoal.—2. *Nascent hydrogen* (sodium-amalgam) converts it into hydro-piperic acid (p. 654) (Foster).—3. *Oil of vitriol* colours it blood-red, and then chars it.—4. When treated with *iodine, bromine,* or *chlorine,* it forms substitution-products.—5. Concentrated *hydriodic acid* acts upon it, even below 100°, producing carbonic acid, and a black, uncrystallisable, humus-like substance (Foster).—6. In contact with *pentachloride of phosphorus*, it acquires a vermillion-red colour, and deliquesces after a few days, forming oxychloride of phosphorus, and yielding vermillion-coloured crystals. If the crystals obtained by the action of pentachloride of phosphorus on piperic acid be mixed with piperidine, a substance is formed which is insoluble in water and potash-ley, but soluble in strong hydrochloric acid, alcohol, and ether.—7. *Nitric acid*, even when dilute, converts piperic acid into an orange-coloured nitro-compound, which, when heated with potassium-hydrate, gives off an odour of coumarin (V. Baho and Keller).—8. Piperic acid added to *fused potassium-hydrate* containing a little water in excess, is at first dissolved; the mixture then turns brown, and gives off hydrogen, and a mass is formed containing protocatechuate [? hypogallate, p. 454], acetate, oxalate, and carbonate of potassium, with a comparatively small quantity of a humus-like body, probably a product of the decomposition of the protocatechuate. The reaction is probably

$$\underset{\text{Piperic acid.}}{C^{12}H^{10}O^4} + 8H^2O = \underset{\text{Protocatechuic acid.}}{C^7H^6O^4} + \underset{\text{Acetic acid.}}{C^2H^4O^2} + \underset{\text{Oxalic acid.}}{C^2H^2O^4} + CO^2 + 7H^2. \text{ (Strecker.)}$$

Piperates.—Piperic acid is monobasic, the general formula of its salts being $C^{12}H^9MO^4$ or $C^{24}H^{18}M''O^8$.

*Piperate of ammonium*, $C^{12}H^9(NH^4)O^4$, forms colourless satiny scales resembling cholesterin. It gives off ammonia slowly in moist air at ordinary temperatures, more quickly between 100° and 150°, and decomposes between 180° and 200°, emitting an odour of anise (V. Baho and Keller).—*Piperate of potassium*, $C^{12}H^9KO^4$, obtained as already described, or by dissolving the acid in potash-ley, forms yellowish-white, silky laminæ, probably belonging to the trimetric system. When heated it glows and emits an odour of anise, and when subjected to dry distillation, yields a small quantity of tar containing phenol, and leaves a mixture of charcoal and carbonate of potassium. It dissolves sparingly in cold, easily in boiling water, sparingly in alcohol, and is nearly insoluble in ether (V. Baho and Keller).—The *sodium-salt* is precipitated on dissolving the acid in hot soda-ley, and cooling, as a white crystalline powder sparingly soluble in cold, easily in hot water, and precipitated from the aqueous solution by alcohol.

The *barium-salt*, $C^{24}H^{18}Ba''O^8$, is obtained by precipitation, as a loosely coherent mass of microscopic needles, dissolving with partial decomposition in about 5,000 pts. of cold water, more soluble in hot water. It is completely decomposed by passing carbonic acid through its aqueous solution. (Foster.)

The *calcium-salt* forms slender needles, somewhat more soluble than the barium-salt. —The *strontium-salt* is a white precipitate. (V. Babo and Keller.)

The *cadmium-salt* is a white powder; the *cobalt-salt* is rose-coloured; the *nickel-salt* is light green and insoluble; the *cupric-salt* is precipitated in slender sky-blue needles on mixing the potassium-salt with cupric sulphate, more abundantly on addition of ammonia.—The *ferrous salt* is yellowish-white, insoluble, easily oxidisable.—The *lead-salt* is a yellowish precipitate, which dissolves slightly when heated, and separates as a white crystalline powder on cooling.—The *magnesium-salt* separates after a few days in slender needles, from moderately dilute solutions of piperate of potassium and chloride of magnesium.—The *manganous-salt* forms small, yellowish, silky laminæ.—The *mercuric-salt* is a yellowish-white precipitate, from which potash separates mercuric oxide.—The *mercurous-salt* is a white precipitate reduced by ammonia.—The *silver-salt*, $C^{12}H^9AgO^4$, is obtained as a colourless, scarcely crystalline powder by precipitating nitrate of silver with piperate of potassium. It is insoluble in water and in alcohol; does not lose weight at 100°.—The *zinc-salt* is a yellowish-white curdy precipitate. (V. Baho and Keller.)

**Hydropiperic acid,** $C^{12}H^{12}O^4$ (G. C. Foster, Chem. Soc. Qu. J. xv. 19; Gm. xv. 11).—This acid, which contains 2 at. hydrogen more than piperic acid, is produced by the action of sodium-amalgam on the latter. When an aqueous solution of potassic piperate is treated with sodium-amalgam at a gentle heat for some hours, the addition of hydrochloric acid precipitates hydropiperic acid in oily drops, which gradually solidify on standing. It may be purified by crystallisation from a large quantity of boiling water, or by solution in alcohol and treatment with animal charcoal.

Hydropiperic acid is colourless; tasteless at first, after a time somewhat burning. As deposited from boiling water, it forms long, exceedingly thin, silky needles; by

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spontaneous evaporation of its ethereal solution, it may be obtained in tolerably large, hard crystals, apparently monoclinic, and mostly hemitropic. It melts at 63° or 64°; solidifies at about 56°; not volatile without decomposition. It is very slightly soluble in cold *water*, somewhat more so in hot water; the hot saturated solution reacts strongly acid; and on cooling deposits the acid in oily drops, as long as its temperature is above the melting point of the latter; the rest separates in long, thin crystals (*vid. sup.*). The acid dissolves in all proportions in *alcohol*, and is very soluble in *ether*.

When *heated* somewhat above its melting point, it gives off white fumes, which, when diluted with much air, smell like oil of anise, and leave a small, easily combustible, carbonaceous acid.—Strong *hydriodic acid* decomposes it, below 100°, into carbonic acid, and a black humus-like body, soluble with black colour in alkalis.—*Fuming nitric acid* colours it blood-red; *ordinary nitric acid* diluted with its own bulk of water, acts violently upon it if gently heated, giving a solution from which water precipitates a semifluid nitro-acid.—*Oil of vitriol* colours it blood-red.—Fused with excess of *hydrated alkali*, it evolves much gas, and the brown fused mass exhibits the reactions of hypogallic acid $C^7H^6O^4$, obtained by the action of hydriodic acid on hemipinic acid (iii. 142, 239); see also DECOMPOSITIONS OF PIPERIC ACID (p. 654).—With *chloride of acetyl* at 150°, it yields hydrochloric acid and a neutral oil, insoluble in water and dilute alkalis.

**Hydropiperates**, $C^{12}H^{11}MO^4$ and $C^{24}H^{22}M''O^8$. The *ammonium-salt*, $C^{12}H^{11}(NH^4)O^4$, crystallises from hot water in small shining scales; it is easily soluble in hot *water*, considerably less soluble in cold. A strong aqueous solution can dissolve more *hydropiperic acid*, forming a solution from which water precipitates the excess of acid, and which gives, if saturated, an almost solid mass of hydropiperate of ammonium, on addition of strong aqueous ammonia.—An *acid potassium-salt*, $C^{24}H^{23}KO^8 = C^{12}H^{11}KO^4.C^{12}H^{12}O^4$, is obtained by boiling a solution of hydropiperic acid in nearly absolute alcohol with dry carbonate of potassium. It crystallises on cooling in hemispherical masses of radiating needles.

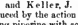
The *barium-salt*, $C^{24}H^{22}Ba''O^8$, crystallises from boiling water in small bunches of needle-shaped crystals.

The *calcium-salt*, $C^{24}H^{22}Ca''O^8$, is prepared by boiling the acid with milk of lime, filtering hot, and separating the excess of lime by carbonic acid; or by precipitating a rather strong solution of the ammonium-salt with chloride of calcium. When purified by crystallisation from a mixture of 2 pts water and 1 pt. alcohol, it forms small needle-shaped crystals, slightly soluble in cold water, more soluble in hot water, but partially decomposed by it. The crystals contain water, which they lose at 100°.

The *silver-salt*, $C^{12}H^{11}AgO^4$, is a crystalline precipitate, almost insoluble in cold water, easily altered by exposure to light, or by solution in hot water.

The hydropiperates of the other metals are mostly precipitates insoluble in cold water.

*Hydropiperate of Ethyl*, $C^{14}H^{16}O^4 = C^{12}H^{11}(C^2H^5)O^4$, is obtained by heating a solution of hydropiperic acid in absolute alcohol saturated with hydrochloric acid for 4 or 5 hours to 130° in a sealed tube, and purified by solution in ether and treatment with animal charcoal. It is a brownish-yellow, neutral liquid; heavier than, and insoluble in, water; not altered by dilute aqueous potash or ammonia, but decomposed by gaseous ammonia, probably with formation of *hydropiperamide*. (**Foster.**)

**PIPERIDINE.** $C^5H^{11}N =$  $\left.\begin{matrix}(C^5H^{10})''\\H\end{matrix}\right\}N$. (**Wertheim**, Ann. Ch. Pharm. lxxv. 58.—**Anderson**, *ibid.* lxxv. 82; lxxxiv. 345.—**Cahours**, Ann. Ch. Phys. [3] xxxviii. 76.—**Von Babo and Keller**, J. pr. Chem. lxxii. 53.—Gm. x. 446; xv. 13.)—A volatile base produced by the action of alkalis on piperine. The production of a volatile base by heating piperine with soda-lime was first noticed by Wertheim and Rochleder, who at first mistook it for aniline, afterwards for picoline. Anderson and Cahours obtained the same base independently of each other, and recognised its separate identity. Its chemical relations have been investigated chiefly by Cahours.

*Preparation.*—1. When 1 pt. of piperine is distilled with 2½ to 3 pts. of potash-lime in a retort connected with a cooled receiver, a distillate is obtained, consisting of water, two distinct volatile bases, and a neutral substance having an agreeable aromatic odour. When this crude liquid is treated with fragments of caustic potash, a light oily substance separates, having a strong ammoniacal odour, and dissolving in water in all proportions. This oil, when distilled, passes over almost wholly between 105° and 108°, but towards the end of the distillation, the thermometer rises quickly to 210°, and there remains stationary. The more volatile product, which forms more than $\frac{9}{10}$ of the crude liquid, distils over entirely at 106° when rectified: this liquid is piperidine (**Cahours**).

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2. Piperine treated with nitric acid evolves red fumes, and forms a substance having an odour of bitter almond oil, and a brown resin, which dissolves with blood-red colour, in potash, and when boiled with that substance, yields piperidine in the form of a volatile liquid (Anderson).—3. Piperine is decomposed, as directed at page 653, by boiling with alcoholic potash, into piperidine and piperate of potassium; and the mother-liquor separated from the crystals of that salt is distilled into a receiver containing hydrochloric acid, whereby hydrochlorate of piperidine is obtained.

*Properties.*—Piperidine is a colourless, very limpid liquid, having a strong ammoniacal odour, but recalling also that of pepper, and a very caustic taste (Anderson). Blues reddened litmus strongly. Boils at 106°. Vapour-density = 2·958 (Cahours); calc. (2 vol.) = 2·946. It dissolves in all proportions in *water*, forming a strongly alkaline liquid which reacts with saline solutions like ammonia, excepting that it does not redissolve the oxides of zinc and copper. Piperidine dissolves also in *alcohol;* it coagulates *white of egg* after a quarter of an hour.

*Nitrous acid* acts violently on piperidine, forming a heavy aromatic liquid. Vapour of *cyanic acid* passed into piperidine forms piperylene-carbamide (piperyl-urea): $C^5H^{11}N + CNHO = C^6H^{12}N^2O$. *Cyanate of methyl* and *cyanate of ethyl* form similar compounds, with 1 at. H replaced by 1 at. methyl or ethyl (see CARBAMIDE, i. 757).—3. With *iodide of methyl, chloride of benzoyl*, &c., it forms substitution-products containing 1 at. of an alcoholic or acid radicle in place of 1 at. hydrogen (p. 657).

*Salts of Piperidine.*—Piperidine saturates the strongest acids, and forms crystalline salts with sulphuric, hydriodic, hydrobromic, hydrochloric, nitric and oxalic acids. (Cahours.)

The *hydrochlorate* forms long colourless needles, easily soluble in water and alcohol, volatilising at a moderate heat and not altered by exposure to the air. The solution forms with *trichloride of gold* small needles of a fine yellow colour, and with *tetrachloride of platinum*, long orange-coloured needles, $2(C^5H^{11}N.HCl).Pt^{iv}Cl^4$, very soluble in water, less soluble in alcohol (Cahours). With *dichloride of platinum* piperidine forms the compound $(C^5H^{11}N)^2Pt''Cl^2$, the solution of which in a large quantity of boiling water deposits the piperidine-compound analogous to Magnus's green ammonio-chloride of platinum. (See PLATINUM-BASES.)

*Hydriodate of Piperidine*, $C^5H^{11}N.HI$, crystallises in long needles resembling the hydrochlorate.—The *nitrate*, $C^5H^{11}N.HNO^3$, forms small needle-shaped crystals.—The *oxalate* forms delicate needles.

*Piperate of Piperidine*, $C^5H^{11}N.C^{12}H^{10}O^4$, is obtained by dissolving piperic acid in aqueous piperidine, as a crystalline pulp, and on dilution, in colourless laminæ having a silky lustre. In contact with the air or with oil of vitriol, it turns yellow from loss of piperidine. It melts at 100° without further alteration, and when strongly heated gives off piperidine and decomposes. When heated for some time to 150°, it becomes partially insoluble in water, but if then dissolved in an alkali, it yields unaltered piperic acid when decomposed by acids. With pentachloride of phosphorus, it behaves like piperic acid. (Babo and Keller.)

The *sulphate*, $(C^5H^{11}N)^2H^2SO^4$, obtained by saturating the base with sulphuric acid, is crystallisable, deliquescent, and very soluble in water. A solution of 1 at. of this salt, boiled with 2 at. cyanate of potassium, yields piperylene-carbamide and sulphate of potassium:

$$[(C^5H^{10})''HN]^2H^2SO^4 + 2\left[\left.\begin{matrix}CO'' \\ K\end{matrix}\right\}N\right] = 2\left[\left.\begin{matrix}(CO)'' \\ \\ H^2\end{matrix}\right\}N\right] + K^2SO^4.$$

***Compound of Piperidine with Carbonic Disulphide***, $(C^5H^{11}N)^2CS^2$, or ***Piperyl-sulphocarbamate of Piperylene-ammonium***, $\left.\begin{matrix}(C^5H^{10})'' \\ (CS)'' \\ C^5H^{12}N\end{matrix}\right\}\begin{matrix}N \\ S\end{matrix}$.—This compound is obtained by carefully dropping sulphide of carbon into piperidine, and crystallising the product from alcohol. It crystallises in slender needles belonging to the monoclinic system.

### *Substitution-derivatives of Piperidine.*

#### α. Containing Alcohol-radicles.

Piperidine exhibits the characters of a secondary monamine, inasmuch as, when heated with the iodide of a monatomic alcohol-radicle, it yields the hydriodate of a volatile ammonia-base, which when separated by potash, and heated with a monatomic alcoholic iodide, unites directly with it, forming an iodide of an ammonium-base. Its formula is therefore probably $\left.\begin{matrix}(C^5H^{10})'' \\ H\end{matrix}\right\}N$.

**Methyl-piperidine.** $C^6H^{13}N = (C^5H^{10})''(CH^3)N$.—The *hydriodate* is obtained by dropping piperidine into an equal volume of cooled iodide of methyl:

$$(C^5H^{10})''HN + CH^3I = (C^5H^{10})''(CH^3)N + HI.$$

The aqueous solution of this salt treated with potash yields the base as a transparent oil of aromatic and ammoniacal odour, soluble in water, boiling at 118°, and having a vapour-density of 3·544; calc. = 3·431.—The *hydrochlorate*, $C^6H^{13}N.HCl$, forms fine colourless needles.—The *chloroplatinate*, $2(C^6H^{13}N.HCl).PtCl^4$, is obtained by spontaneous evaporation of its alcoholic solution, sometimes in needles, sometimes in orange-coloured plates. (Cahours.)

*Iodide of Dimethyl-piperylene-ammonium*, $C^7H^{16}NI = (C^5H^{10})''(CH^3)^2NI$.—Methyl-piperidine and iodide of methyl heated together for some days to 100° in a sealed tube, unite and form this compound, which separates from alcohol in fine crystals, and when heated, either alone or with solid potash, partly volatilises undecomposed, and is partly resolved into methylic iodide and methyl-piperidine. (Cahours.)

**Ethyl-piperidine.** $C^7H^{15}N = C^5H^{10}(C^2H^5)N = (C^5H^{10})''(C^2H^5)N$.—The *hydriodate*, prepared like the corresponding methyl-compound, yields the base by distillation with potash, as a colourless mobile oil, less aromatic than methyl-piperidine; lighter than water, in which it is less soluble than methyl-piperidine, easily soluble in alcohol and ether. Boils at 128°. Vapour-density, obs. = 3·986; calc. = 3·917.

The *hydrochlorate*, $C^7H^{15}N.HCl$, forms beautiful highly lustrous needles.—The *chloroplatinate*, $2(C^7H^{15}N.HCl).PtCl^4$, crystallises from warm aqueous alcohol in very beautiful orange-coloured crystals.

*Iodide of Diethyl-piperylene-ammonium*, $C^9H^{20}NI = (C^5H^{10})''(C^2H^5)^2NI$.—Obtained like the corresponding methyl-compound, as a viscid mass, which dissolves in all proportions in water, but does not crystallise. In contact with oxide of silver, it yields iodide of silver, and a bitter alkaline solution which yields by evaporation, deliquescent crystals of *hydrate of diethyl-piperylene-ammonium*, resolvable by heat into ethyl-piperidine and a combustible gas. This hydrate dissolves in hydrochloric acid, and the solution when evaporated yields deliquescent crystals of the *hydrochlorate*.—The *chloroplatinate*, $2C^9H^{20}NCl.PtCl^4$, is precipitated on mixing the hydrochlorate with aqueous tetrachloride of platinum, or crystallises on cooling from a mixture of the boiling dilute solutions, in small orange-coloured crystals resembling chloroplatinate of potassium. (Cahours.)

**Amyl-piperidine,** $C^{10}H^{21}N = (C^5H^{10})''(C^5H^{11})N$.—Prepared like the preceding compounds. Colourless oil, boiling at 186°, and smelling like ammonia and fusel-oil. Vapour-density, obs. = 5·477; calc. = 5·373. It is less soluble in water than methyl- or ethyl-piperidine; forms crystallisable salts with most acids. The *hydriodate*, $C^{10}H^{21}N.HI$, crystallises in broad, white, shining laminæ. The *chloroplatinate*, $2(C^{10}H^{21}N.HCl).PtCl^4$, crystallises from warm moderately dilute alcohol in very hard prisms of a fine orange colour. (Cahours.)

### β. Containing Acid-radicles.

**Benzopiperide,** $C^{12}H^{15}NO = C^5H^{10}(C^7H^5O)N$.—By treating piperidine with chloride of benzoyl, a heavy oil is obtained which, when treated with acidulated water, yields hydrochlorate of piperidine, while benzopiperide remains undissolved, and quickly solidifies. When purified, by recrystallisation from alcohol, it forms beautiful colourless prisms.

**Cumyl-piperide,** $C^{15}H^{21}NO = C^5H^{10}(C^{10}H^{11}O)N$, obtained like the preceding, by the action of chloride of cumyl on piperidine, forms beautiful tabular crystals.

**PIPERIDINE-UREA.** See CARBAMIDES (i. 757).

**PIPERINE.** $C^{17}H^{19}NO^3$. (Oersted, Schw. J. xxix. 80.—Pelletier, Ann. Ch. Phys. [2] xvi. 344; li. 199.—Merck, Trommsd. N. J. xx. 1, 34.—Wackenroder, Br. Arch. xxxvii. 347.—Duflos, Schw. J. lxi. 22.—Varrentrapp and Will, Ann. Ch. Pharm. xxxix. 283.—Th. Wertheim, *ibid.* lxx. 58.—Gerhardt, Compt. Chim. 1849, p. 375; Ann. Ch. Phys. [3] vii. 253.—Anderson, Ann. Ch. Pharm. lxxv. 82; lxxxiv. 345.—Cahours, Ann. Ch. Phys. [3] xxxviii. 76.—Stenhouse, Ann. Ch. Pharm. xcv. 106.—Von Babo and Keller, J. pr. Chem. lxxii. 53.—Strecker, Ann. Ch. Pharm. cv. 317.—Gm. xv. 19.—Gerh. iv. 93.)

This alkaloïd, discovered by Oersted in 1819, exists in long and black pepper (*Piper nigrum* and *P. longum*), also, according to Stenhouse, in the black pepper of Western Africa, *Cubeba Clusii*, which does not contain cubebin. According to Landerer (Vierteljahrschr. pr. Pharm. xi. 72), it exists also in the berries of *Schinus mollis*, a tree belonging to the terebinthaceous order.

*Preparation.*—White pepper is exhausted with alcohol of specific gravity 0·833; the tincture is distilled to an extract; and this extract is mixed with potash-ley, which dissolves the resin and leaves a green powder. The latter is washed with water, dissolved in alcohol of specific gravity 0·833 and crystallised. By repeated crystallisation the piperine is obtained colourless (Poutet, J. Chim. med. i. 531; Berzel. Lehrb. 3 Aufl. vii. 577).—Stenhouse dissolves the extract of cubebs, prepared with wood-spirit, in alcohol, and mixes it with strong potash-ley, whereupon a brown oil separates, which yields crystals on standing. The mother-liquor, if again mixed with alcohol, yields another portion of oil, which likewise deposits crystals on standing. These crystals are purified by pressure and recrystallisation.

Winckler (Mag. Pharm. xviii. 153) distils the alcohol from the alcoholic tincture of long pepper; dissolves the residue in the required quantity of hot alcohol; precipitates the solution with basic acetate of lead; mixes the filtrate while warm with as much sulphuric acid as is necessary to precipitate the lead; filters while warm; distils the alcohol from the filtrate; exhausts the residue with water; and dissolves the undissolved portion in hot alcohol, whereupon piperine crystallises on cooling.

Impure piperine may be purified by washing with absolute alcohol, or better with weak potash-ley. (Henry and Plisson.)

*Properties.*—Piperine crystallises in colourless monoclinic prisms, exhibiting the combination ∞P . oP, sometimes with [ ∞P∞ ]. Ratio of $a : b = 1·468 : 1$. Angle of inclined axes $b, c = 70° 42'$. Angle ∞P : ∞P (orthod.) = 84° 30'; oP : ∞P = 75° 50' (Kopp). It melts at about 100° (Pelletier), at 100° or above (Wackenroder), to a pale yellow limpid oil, which solidifies on cooling to a pale yellow transparent, strongly refracting resin. The specific gravity of fused piperine is 1·1931 at 18°. (Wackenroder.)

Piperine is insoluble in cold, very slightly soluble in boiling water; soluble in alcohol, especially when warm, less soluble in ether. The alcoholic solution has a very hot taste like that of pepper. It dissolves also in volatile oils and in acetic acid, but not in alkalis. The solutions have no action on polarised light.

| *Calculation.* | | | Liebig. | Pelletier. | Regnault. *mean.* | Gerhardt. *mean.* | Laurent. | Stenhouse. *mean.* |
|---|---|---|---|---|---|---|---|---|
| $C^{17}$ | 204 | 71·58 | 69·78 | 69·47 | 71·19 | 71·52 | 71·66 | 71·72 |
| $H^{19}$ | 19 | 6·67 | 6·69 | 6·80 | 6·78 | 6·68 | 6·66 | 6·66 |
| N | 14 | 4·91 | 4·09 | 4·51 | 4·94 | 4·81 | . . | 4·76 |
| $O^3$ | 48 | 16·84 | 19·44 | 19·22 | 17·09 | 16·99 | . . | 16·86 |
| $C^{17}H^{19}NO^3$ | 285 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | | 100·00 |

Will and Varrentrapp found 4·56 per cent. nitrogen. Regnault (Ann. Ch. Phys. [2] lxviii. 158) first gave the correct formula, which was corroborated by Laurent (*ibid.* [3] xix. 363), and finally settled by Strecker's investigation. Older formulæ: $C^{40}NH^{24}O^8$ (Pelletier); $C^{40}NH^{22}O^8$ (Liebig, Ann. Ch. Pharm. vi. 36); $C^{70}N^2H^{38}O^{12}$ (Gerhardt); $C^{70}N^2H^{39}O^{12}$ (Wertheim); $C^{70}N^2H^{40}O^{12}$ (v. Babo and Keller). Compare also O. Henry and Plisson (J. Pharm. xvii. 449).

*Decompositions.*—1. Piperine blackens by dry distillation, and yields a brown empyreumatic oil, from which carbonate of ammonium crystallises (Gmelin).—2. Heated in a platinum spoon, it melts like wax, takes fire at a stronger heat, and leaves an easily combustible charcoal (Merck).—3. Piperine suspended in acidulated water and exposed to the action of the *electric current*, is violently attacked, as also by hot concentrated *nitric acid* (Hlasiwetz and Rochleder, Wien. Akad. Ber. v. 447).—It is coloured blood-red by *oil of vitriol*, loses this colour on addition of water, and, if the action of the oil of vitriol has not been continued for a very long time, does not appear to be sensibly altered (Pelletier). *Bromine* converts piperine into a peculiar, non-crystalline product (Gerhardt). *Iodine* acts upon it only when the two are fused together, forming a dark black-brown mass, which hardens on cooling (Wackenroder).—6. *Nitric acid* colours piperine greenish-yellow, orange, and then red; dissolves it with a yellow colour, the solution yielding dirty yellow flakes when mixed with water; and on further action, produces oxalic acid, together with a yellow artificial bitter (Pelletier, Oersted, Wackenroder). Strong nitric acid forms an orange-red resin, which partly dissolves with deepening colour when heated. The solution no longer yields piperine when treated with water or alkalis (Duflos). The brown resin which is produced from piperine by nitric acid, with violent action, evolution of nitrous acid, and the odour of bitter almond-oil, assumes a splendid blood-red colour when treated with hydrate of potassium, and when boiled therewith yields a distillate of piperidine (Anderson). Von Babo and Keller, by treating piperine with *nitrous acid*, and subsequently distilling it with potash-ley, obtained volatile needles which had the odour of coumarin, melted in boiling water, dissolved in alcohol and ether, and, after fusion with hydrate of potassium, gave the reaction of salicylic

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acid with ferric chloride.—7. By boiling with *alcoholic potash*, piperine is converted into piperidine and piperate of potassium (p. 653). When distilled with *potash-lime* it yields piperidine, together with other products. If the temperature does not rise above 150°—160°, no ammonia is given off, and the brown residue contains an azotised acid which may be separated by hydrochloric acid; it is yellow, resinous, and becomes strongly electric by friction. If the mixture of piperine and lime is heated to 200°, it gives off ammonia, and the residue often contains an uncrystallisable non-azotised acid (Wertheim). Piperine heated with *hydrate of potassium* melts, gives off a sharp odour of pepper, and yields a milky aqueous distillate; at a stronger heat, it gives off hydrogen and finally ammonia (Gerhardt).—8. Piperidine heated with *acid chromate of potassium* and *sulphuric acid* gives off a large quantity of carbonic anhydride and yields a slightly acid aqueous distillate which reduces nitrate of silver (Gerhardt). 9. *Permanganate of potassium* added to a solution of piperine mixed with sulphuric acid, colours it green after a few hours (Duflos).—10. *Phosphomolybdic acid* colours piperine brown-yellow, and precipitates it in flocks (Sonnenschein). Piperine also forms a yellow precipitate with *phosphantimonic acid* (p. 498).

Salts of Piperine. Piperine is but a weak base, and does not form salts with all acids.

*Hydrochlorate.*—Piperine absorbs from 13·0 to 13·7 per cent. hydrochloric acid gas, forming a product which melts and crystallises on cooling, dissolves in alcohol, but is decomposed by water.

The *chloromercurate*, $2C^{17}H^{19}NO^{3}.HCl.Hg''Cl^{2}$, is obtained by mixing a solution of 1 pt. piperine in strong alcohol slightly acidulated with hydrochloric acid, and 2 pts. of mercuric chloride also dissolved in alcohol, and leaving the mixture at rest for several days. It then deposits the mercury-salt in yellow, shining, transparent, triclinic crystals which become darker when exposed to the air or heated to 100°. (For details of the crystalline form, see Schabus, *Bestimmung der Krystallgestalten*, &c., p. 198; also Gm. xv. 23.) The salt is insoluble in water, slightly soluble in strong hydrochloric acid and in cold alcohol, more soluble in boiling alcohol.

*Chloroplatinate*, $4C^{17}H^{19}NO^{3}.2HCl.Pt^{iv}Cl^{4}$.—Obtained in large, roseate, monoclinic crystals, by mixing a concentrated alcoholic solution of piperine with a concentrated alcoholic solution of platinic chloride acidulated with strong hydrochloric acid. It is very slightly soluble in water, and appears to be partially decomposed by a large quantity; moderately soluble in boiling alcohol, whence it separates on cooling as an orange-coloured crystalline powder. It may be dried at 100° without alteration, but melts and decomposes with intumescence at a higher temperature.

*Iodide of Piperine.*—Piperine unites with iodine, forming shining, bluish-black needles, soluble in alcohol and containing $4C^{17}H^{19}NO^{3}.I^{3}$. (Weltzien, *Zusammenstellung*, p. 562)

**PIPERITÆ, OLEUM MENTHÆ,** volatile oil of peppermint, is prepared by distilling the herb of *Mentha piperita* with water. It is a transparent, usually colourless, but sometimes greenish oil, very mobile, having a pungent odour and an aromatic burning taste with cooling after-taste. Specific gravity = 0·902—0·91 (Blanchet and Sell); 0·899 after several rectifications (Kane): 0·9028 at 14·5° (Gladstone). For the refractive and optical rotatory power, according to Gladstone, see OILS, VOLATILE (p. 189). Boiling point 188°—193° (Kane). When exposed to cold, or submitted to fractional distillation it deposits Peppermint-camphor or Menthol, $C^{10}H^{20}O$ (iii. 880), in quantities varying according to its origin. The permanently liquid portion of the oil has the composition $C^{12}H^{20}O$, according to Blanchet and Sell; $C^{21}H^{40}O^{2}$, according to Kane (J. pr. Chem. xx. 439).

**PIPERYLENE-CARBAMIDE.** *Piperyl-carbamide* or *Piperyl-urea.* (See CARBAMIDE, i. 757.)

**PIPERYLENE-SULPHOCARBAMIC ACID.** See PIPERIDINE (p. 656).

**PIPESTONE.** A variety of clay-slate.

**PIPETTE.** A vessel with a bulb and narrow neck used for transferring liquids (See ANALYSIS, VOLUMETRIC, i. 256.)

**PIRENEITE.** Iron lime-garnet.

**PIROPE.** Syn. with PYROPE.

**PISANITE.** A native sulphate of copper and iron found in a cave near a bed of cupriferous pyrites in Turkey. It gave by analysis 15·56 per cent. $Cu''O$, 10·98 $Fe''O$, 29·90 $SO^{3}$ and 43·56 water, agreeing with the formula $(Cu\,;\,Fe)''SO^{4}.7H^{2}O$. (Pisani, Jahresb. 1859, p. 811.)

**PISOLITE.** Syn. with PEASTONE (p. 360.)

**PISSOPHANE.** An amorphous or stalactitic mineral occurring at Garnsdorf near Saalfeld, and at Reichenbach in Saxony, consisting of basic aluminico-ferric sulphate. Hardness = 1·5. Specific gravity 1·93—1·98. It is transparent, with olive-green colour and vitreous lustre; very fragile and exhibits a conchoïdal fracture. It has been analysed by Erdmann (Schw. J. lxii. 104), with the following results:

| | $Al^2O^3$. | $Fe^2O^3$. | $SO^3$. | $H^2O$. | Gangue and loss. | | |
|---|---|---|---|---|---|---|---|
| 1. *Green* . . . | 35·16 | 9·74 | 12·70 | 41·69 | 0·71 | = | 100 |
| 2. " . . . | 35·30 | 9·80 | 12·49 | 41·70 | 0·70 | = | 100 |
| 3. *Yellow* . . . | 6·80 | 40·06 | 11·90 | 40·13 | 1·11 | = | 100 |

Nos. 1 and 2 are probably $3M^2O^3.SO^3.15H^2O$ or more exactly $5M^2O^3.2SO^3.30H^2O$; No. 3 is $2M^2O^3.SO^3.15H^2O$. (Dana, ii. 390.)

**PISTACIA.** The berries of *Pistacia Lentiscus*, a terebinthaceous plant common in Algeria, yield when comminuted and boiled with water, from 20 to 25 per cent. of a dark green sharp-tasting fat, which melts completely at 32°—34°, and may be resolved, by partial solidification and decantation of the still fluid portion, into a white crystalline fat melting at 34°—35°, and a dark green fat remaining fluid at 0°. (Leprieur, Rép. Chim. app. ii. 328.)

**PISTACITE.** Lime and iron epidote (ii. 390.)

**PISTOMESITE.** Syn. with MESITIN-SPAR (iii. 928).

**PITCH.** *Poix. Pech.* This term is applied to a variety of solid resinous substances which are generally of a dark colour and brilliant lustre. The common kinds of pitch are obtained from some one or other of the various kinds of tar produced in the destructive distillation of wood, coal, &c., and are prepared by evaporating off from the tar, the liquid oily substances mixed with the solid resinous matters, until the residuum has the desired consistence.

A certain amount of pitch may in this way be obtained from all kinds of tar; but as a rule, the tar produced in destructive distillation at high temperatures, and that obtained from highly resinous wood and from caking coal, even at comparatively low degrees of heat, contains a much larger proportion of the solid resinous substances which constitute pitch, than the tar produced at a low red heat, or obtained from bituminous minerals which do not cake or undergo a kind of partial fusion when heated. (See TAR.)

Pitch is generally prepared either from Archangel, Stockholm and American tar, or from that kind of coal-tar produced in the manufacture of illuminating gas. Besides these kinds there are several varieties of pitch which occur native and are commonly termed mineral pitch. (See ASPHALT, i. 425.)

Little is known of the chemical history of the several varieties of pitch; but in general their constitution is probably more or less analogous to that of other resins, and like these latter, they present specific differences in their behaviour with solvents, &c. Another kind of pitch, called *Burgundy pitch*, is employed in medicine, and is the melted resin of *Abietis resina* or *Thus*. It is of a yellowish-white colour. B. H. P.

**PITCH, MINERAL.** Syn. with BITUMEN.

**PITCHBLENDE.** Native oxide of uranium (see URANIUM).

**PITCHSTONE.** A felspathic rock (ii. 623) containing excess of silica, and having a pitchy rather than a glassy lustre.

**PITCHY IRON ORE.** A term applied sometimes to triplite (p. 571), sometimes to pitticite (*infra*), sometimes to a variety of brown hæmatite.

**PITKÄRANTITE.** A dark green mineral from Pitkäranta in Finland, consisting of an altered hornblende, occurring, according to Scheerer, in crystals having the form of augite, and splitting into thin plates parallel to the orthodiagonal. Contains, according to an analysis by R. Richter: 61·25 per cent. $SiO^2$, 0·41 $Al^2O^3$, 12·71 $Fe''O$, 0·83 $Mn''O$, 13·30 $Mg''O$, 9·17 $Ca''O$ and 2·52 water. (*Rammelsberg's Mineralchemie*, p. 498.)

**PITOYINE.** An alkaloïd obtained, according to Peretti (J. Pharm. Oct. 1835, p. 513), from *China Pitoya*, which is probably identical with *China bicolor* or *Ch. Tecames*. It is soluble in water, alcohol, and ether, and has a slightly bitter taste, which is stronger in the aqueous or alcoholic solutions of its salts. It melts at 100°, and partly volatilises at a higher temperature in very bitter vapours which condense in prismatic crystals. It is decomposed by hot strong nitric acid. It is said to be a febrifuge. (Handw. d. Chem. vi. 540.)

**PITTACAL** (from *πίττα*, pitch, and *καλός*, ornament or beauty). One of the numerous substances discovered by Reichenbach in the course of his researches on the oils produced by the distillation of wood-tar. Its composition is unknown. It is obtained by acting on the heaviest or least volatile portion of the oil first with potash, until the free acids are nearly neutralised, and then with baryta-water. In this manner a deep blue colour is formed. This blue substance is pittacal, probably in a very impure condition. In the solid state it possesses a coppery or bronze-like lustre; but this property is not characteristic, as it is shared, not only with almost all coal-tar colours, but also with indigo and prussian-blue.

Pittacal appears to have decided basic characters, for it is dissolved by acids and precipitated by alkalis. It is tasteless, inodorous, and not volatile without decomposition. It is insoluble in water, alcohol, or ether, and no process is known by which it can be separated from other substances, or its purity ascertained. It forms a species of lake with alumina, and is said to dye a fast blue on vegetable tissues mordanted with tin or alumina. Its acid solutions are reddish; but, when diffused in water, it is said to have a greenish tint.

In many of its reactions, it resembles the colouring matters formed by acting with oxide of silver or alkalis on the iodides of the ammonium-bases derived from certain tertiary monamines. Indeed the late Dr. Gregory in the last edition of his "Organic Chemistry" (p. 471), suggests that the beautiful coloured compounds obtained by treating iodide of ethyl-chinolyl-ammonium with oxide or sulphate of silver, may be identical or homologous with pittacal. But it must not be forgotten that those colours were yielded only by the bases derived from the products of the distillation of cinchonine, and that the same products cannot be procured from the isomeric bases of the leucoline series. On the other hand, the reactions which occur during the formation of the blue obtained by acting on a solution of iodide of pelamine (iii. 573) with potash or ammonia, remarkably resemble the phenomena observed in the production of pittacal. (See AMYL-CHINOLINE, i. 873.) The insolubility in alcohol appears to be the chief distinction between pittacal and the coloured derivatives from coal-tar or cinchonine.

On treating the heaviest bases from coal-tar with solid potash in the process for rendering them anhydrous, the fluid (ascertained to be free from copper) often becomes of a light blue colour, which seems to indicate the presence of a substance allied to the body from which pittacal is derived.

The interest attaching itself to pittacal is rather increased than lessened by the researches which have been made upon the colouring matters of coal-tar, because they appear to show that wood-tar may eventually become a source of new colours. At the same time, the comparatively small amount of nitrogen in wood, while limiting the formation of alkaloïds, points to the heavier and less known non-basic oils as the chief source of new derivatives. C. G. W.

**PITTICITE.** *Pittizite. Iron sinter. Diarsenate of Iron. Pitchy Iron ore. Eisenpecherz.*—An arsenato-sulphate of iron occurring in reniform masses, having a yellowish or reddish-brown, blood-red, or white colour, yellow streak and vitreous lustre; translucent to opaque; hardness = 2 to 3; specific gravity = 2·2 to 2·5.

*Analyses.*—*a.* From Freiberg (Stromeyer, Gilb. Ann. lxi. 181).—*b.* From Schwarzenberg in Saxony (Rammelsberg, Pogg. Ann. lxxii. 139).—*c, d.* From Sieglitzstollen in the Radhausberg, near Gastein: yellow (Rammelsberg):

|  | $As^2O^5$. | $SO^3$. | $Fe^2O^3$. | $Mn^2O^3$. | $H^2O$. |  |  |
|---|---|---|---|---|---|---|---|
| *a.* | 26·06 | 10·04 | 33·10 | 0·64 | 29·26 | = | 99·10 |
| *b.* | 26·70 | 13·91 | 34·85 | . . | 24·54 | = | 100 |
| *c.* | 24·67 | 5·20 | 54·66 | . . | 15·47 | = | 100 |
| *d.* | 28·45 | 4·36 | 58·00 | . . | 12·59 | = | 103·40 |

These analyses show that the mineral is of varying composition. Analysis *a* may be represented by the formula $(3Fe^2O^3.2As^2O^5).(Fe^2O^3.2SO^3).30H^2O$; which contains the same salts as diadochite; *b* by $(3Fe^2O^3.2As^2O^5).(Fe^2O^3.3SO^3).24H^2O$, containing 1 at. $SO^3$ more than the preceding; *c* and *d* are mixtures.

**PITTINITE.** An impure variety of pitchblende.

**PLAGIONITE.** A sulphantimonite of lead occurring at Wolfsberg in the Hartz, in monoclinic crystals having the axes $a : b : c = 0·8802 : 1 : 0·37015$. Angle of inclined axes = 72° 28′. $\infty P : \infty P = 85° 25′$; $oP : [P\infty] = 158° 9′$. Observed combination, $2P . oP . P . \infty P\infty$. The crystals are thick tabular; the face oP shining and smooth, the others striated. Cleavage parallel to 2P, perfect. The mineral occurs also massive, granular. Hardness = 2·5. Specific gravity = 5·4. Lustre metallic. Colour blackish lead-grey. Opaque. Brittle. Before the blowpipe it decrepitates and melts easily, giving off fumes of sulphur and antimonious oxide, and coating the charcoal with oxide of lead.

According to an analysis by H. Rose (Pogg. Ann. xxviii. 428), it contains 21·53 per cent. sulphur, 37·94 antimony, and 40·52 lead, agreeing most nearly with the formula $Pb^5Sb^8S^{17} = 5Pb''S.4Sb^2S^3$, which requires 21·10 per cent. sulphur, 37·86 antimony, and 40·74 lead.

**PLANERITE.** A mineral consisting of hydrated aluminic phosphate with cupric and ferric hydrates, occurring in fissures of disintegrated quartz at Gumeschefsk in the Ural, in botryoïdal aggregations having an indistinct fibrous structure, a green colour in the recent state, translucent on the edges. Specific gravity = 2·65. It is but slightly attacked by acids, but easily by caustic potash or soda, which dissolves the phosphate of aluminium, leaving a brown residue. Analysis gave 33·94 per cent. $P^2O^5$, 37·48 $Al^2O^3$, 3·78 $Cu''O$, 3·52 $Fe''O$ and 20·93 $H^2O$ (= 99·59), answering to the formula $4(3Al^2O^3.2P^2O^5.9H^2O).3(Cu\,;\,Fe)''H^2O^2$. (R. Hermann, Jahresb. 1862, p. 764.)

**PLANTAGO.** The ash of the sea-side plantain (*Plantago maritima*) has been analysed by E. Harms (Jahresb. 1858, p. 511). 100 pts. were found to contain 4·97 per cent. sulphuric anhydride, 0·58 phosphoric anhydride, 3·76 silica, 2·28 ferric phosphate, 1·13 aluminic phosphate, 62·53 chloride of sodium, 10·37 chloride of potassium, 4·71 magnesia, 6·59 lime, and 3·08 potash. 100 pts of the green plant yielded 79·52 pts. water; 100° pts. of the fresh plant gave 3·91 per cent. ash; of the plant dried at 100°, 19·12 pts.

**PLANTS, CHEMISTRY OF.** See PHYTO-CHEMISTRY (p. 636).

**PLASMA.** A faint translucent chalcedony, approaching jasper, having a greenish colour sprinkled with yellow and whitish dots, and a glistening lustre.

The term *plasma* is also applied to the simplest form of organised matter in the vegetable or animal body, out of which the several tissues are formed.

**PLASMIN.** A name applied by Denis (Compt. rend. lii. 1239; Jahresb. 1861, p. 725) to a constituent of the blood to which he supposes the property of spontaneous coagulation to be due. It is extracted from perfectly fresh blood, by adding a saturated solution of sulphate of sodium ($\frac{1}{6}$ of the vol. of human blood), filtering the supernatant liquid from the blood-globules after some hours, and saturating it with pulverised chloride of sodium. The plasmin then separates in flocks. It is soluble in water, is not altered by careful drying at 40°, but loses its solubility in water when heated to 100°, or by contact with acids and alkalis, even when very dilute. The solution in 15 to 20 pts. water solidifies after a few minutes to a colourless transparent jelly, which by pressure between paper is converted into fibres of fibrin.

**PLASTER.** A pharmaceutical term for lead-soaps (iii. 560).

**PLASTER OF PARIS.** Gypsum heated and ground up. It is thereby rendered anhydrous, and when subsequently mixed with water, quickly takes up the water of hydration which it has lost, and is converted into a hard substance which expands in solidifying, so that it accurately fits into any mould into which the pasty mixture is poured; hence it is much used for taking casts of statues, medals, &c. (See GYPSUM, ii. 963.)

**PLATA AZUL.** A term applied in the Mexican mines to an ash-grey or black mineral regarded as carbonate of silver; also called SELBITE.

**PLATA VERDE.** Native bromide of silver. (See SILVER.)

**PLATAMMONIUM.** A hypothetical base, $N^2H^6Pt''$, supposed to exist in the diammonio-platinous compounds. (See PLATINUM-BASES.)

**PLATARSENETHYLIUM.** $As^2(C^2H^5)^6Pt''$. (See ARSENIC-RADICLES, ORGANIC, i. 400.)

**PLATINA.** The old name of Platinum.

**PLATINIC** and **PLATINOUS COMPOUNDS.** (See PLATINUM, p. 666.)

**PLATINUM.** *Atomic weight* 197·4. *Symbol Pt.* This metal was discovered in the auriferous sand of certain rivers in America. Its name is derived from the Spanish word *platina*, a diminutive of *plata*, silver, and was applied to it on account of its whiteness. It occurs in the form of rounded or flattened grains of a metallic lustre. It has been found in Brazil, Mexico, California, Oregon, St. Domingo, and on the eastern declivity of the Ural chain; in small quantity also in certain copper-ores from the Alps; it is everywhere associated with the debris of a rock, easily recognised as belonging to one of the earliest volcanic formations.

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The grains of native platinum contain from 75 to 87 per cent. of that metal, a quantity of iron generally sufficient to render them magnetic, from ½ to 1 per cent. of palladium, but sometimes much less, with smaller quantities of copper, rhodium, osmium, iridium, and ruthenium. To separate the platinum from these bodies, the ore is digested in a retort with hydrochloric acid, to which additions of nitric acid are made from time to time. When the hydrochloric acid is nearly saturated, the liquid is evaporated in the retort to a syrup, then diluted with water, and drawn off from the insoluble residue. If the mineral is not completely decomposed, more nitro-muriatic acid is added and the distillation continued. A portion always remains undissolved, consisting of grains of a compound of osmium and iridium (iii. 324; iv. 240), and little brilliant plates of the same alloy, besides foreign mineral substances which may be mixed with the ore. The solution is generally deep red, and emits chlorine from the presence of tetrachloride of palladium; to decompose which, the liquid is boiled, whereupon chlorine escapes, and the palladium is reduced to dichloride. Chloride of potassium is then added, which precipitates the platinum as a sparingly soluble double chloride of platinum and potassium, leaving the palladium in solution. The precipitate, which has a yellow colour if pure, but red if it is accompanied by the double chloride of iridium and potassium, is collected on a filter, and washed with a dilute solution of chloride of potassium. By igniting this double salt with twice its weight of potassic carbonate the platinum is reduced to the metallic state, while a portion of the iridium remains as trioxide. The soluble potassium salts are then removed by washing with hot water, and the platinum is dissolved by nitro-muriatic acid, which leaves the trioxide of iridium undissolved. To complete the separation of the iridium, the precipitation by chloride of potassium and ignition with carbonate of potassium may require to be repeated several times. The platinum-solution thus freed from iridium is mixed with sal-ammoniac, which throws down a yellow precipitate of the double chloride of platinum and ammonium. From this precipitate, when heated to redness, chlorine and sal-ammoniac are given off, and the platinum remains in the form of a loosely coherent mass, called *spongy platinum*. When it is not required to have platinum absolutely pure, the solution first obtained from the ore is precipitated by sal-ammoniac, and the precipitate is treated in the manner just described: much of the platinum of commerce is obtained in this way. The small trace of iridium which is left in commercial platinum greatly increases its hardness and tenacity.

Platinum is too refractory to be fused in coal furnaces: but at a high temperature its particles cohere like those of iron, and it may, like that metal, be welded and thereby rendered malleable. For this purpose the spongy platinum obtained by igniting the chloroplatinate of ammonium, is rubbed to powder very gently between the hands, pressed through a linen bag, and the coarser particles which remain in the bag are triturated in a wooden mortar with a wooden pestle, not with any harder substance, because the platinum would then acquire the metallic lustre, and would not weld so easily as in the contrary case. The powder is finally triturated with water, and the finer particles separated from the coarser by elutriation. The whole of the finer powder is then mixed up with water to a uniform paste, and pressed into a brass cylinder 6¾ inches high, 1·12 inch in diameter at top, and 1·23 at bottom, and having its lower and wider end accurately closed with a steel stopper, which goes in ¼ of an inch, and is wrapped round with bibulous paper, by which the running off of the water is facilitated. The interior of the cylinder is smeared with grease, and the cylinder being placed in a glass full of water, is itself filled with water, and then completely filled with the platinum-paste. In this manner all cavities and inequalities are avoided. On the platinum-paste is laid, first a sheet of blotting-paper, then a layer of woollen cloth, and part of the water is pressed out of it by means of a wooden cylinder held in the hand. A plate of copper is then laid upon the paste, so that the cylinder may be introduced in a horizontal position into a very powerful lever-press, in which a stamp presses on the copper plate. After the pressure, the steel stopper, which closes the lower end of the cylinder, is taken out, and after it the now solid cake of platinum. The cake is heated to redness to drive off the remaining water and the grease, and render it more compact. It is then placed in an air-furnace having a very strong draught and fed with good coke, and exposed for twenty minutes to an intense heat, which is diminished during the last five minutes. In the furnace, the cake is laid by one of its ends on a plate of refractory clay strewn with pure sand, and placed 2½ inches above the grate, and a cylindrical pot is inverted over it in such a manner as not to touch the platinum at any point. The cake, while still red hot, is taken from the furnace, laid down on one of its bases, and struck repeatedly on the other with a heavy hammer. Should it bend, it must not on any account be hammered on the side, as that would break it, but must be straightened by well-directed blows on the ends. When the cake has been sufficiently condensed by this treatment, it may be brought into any required form by heating and hammering, just like any other ductile metal. If the platinum has become covered, while in the fire, with ferruginous scales, it must be coated with a moist mixture of equal measures of borax and cream of tartar; heated to redness in an air-furnace on a platinum tray, over which an earthen pot is inverted; and immersed, while still hot, in dilute sulphuric acid, which dissolves the flux in a few hours.—The specific gravity of the cake (with its interstices), after pressure, is about 10·0; after strong ignition, from 17·0 to 17·7; after hammering, 21·25; after drawing out into thick wire, 21·4; and after drawing out into very thin wire, 21·5. (Wollaston.)

Commercial platinum prepared as above described is never quite pure, always retaining small quantities of osmium and silicium. To free it from these impurities, and at the same time to render it more compact and free from pores, Deville and Debray fuse it by means of a hydrogen or coal-gas flame fed with oxygen, in the lime-furnace represented in figures 733, 734 (p. 312). The osmium is then driven off as osmic tetroxide and the silicium passes to the state of calcic silicate, which melts to a colourless bead, and is ultimately absorbed by the walls of the furnace. Iron and copper also, if present in the platinum, are oxidised and form fusible slags, which are absorbed by the lime.

Deville and Debray have likewise introduced the following new process for the extraction of platinum from its ores in the dry way. A small reverberatory furnace, the bed of which is composed of a hemispherical cavity of fire-brick lined with clay, is heated to full redness, and a charge, consisting of 2 cwt. of the platinum ore mixed with an equal weight of galena, is added in small quantities, stirring with iron rods till the platinum and lead ores have combined into a matt. A small quantity of glass is thrown in to act as a flux, and by degrees a quantity of litharge is added equal in weight to the galena. The sulphur of the galena is thereby completely oxidised and expelled, whilst the lead of the galena and the litharge is reduced to the metallic state, and unites with the platinum, forming an easily fusible alloy. On leaving the melted mass at rest for some time, the osmide of iridium (which is not attacked during the operation) gradually sinks to the bottom of the liquid alloy; the upper portions of the platiniferous lead are then cautiously decanted from it by iron ladles and cast into ingot-moulds. The residue containing the osmide of iridium is added to a subsequent melting.

The platiniferous lead is now submitted to cupellation in the ordinary way, and the crude metallic platinum left after cupellation, is refined by fusion on a bed of lime as above described. The platinum thus obtained is nearly pure, and very ductile and malleable.

An alloy of platinum, iridium, and rhodium, better adapted for some purposes than pure platinum, because it is harder, bears a higher temperature without fusing, and is less easily attacked by chemical reagents, may be obtained by simply fusing the platinum-ore in the oxyhydrogen flame on a bed of lime, with a quantity of lime equal in weight to the amount of iron in the ore. Palladium and osmium are volatilised during the fusion, while the copper and iron are oxidised, and form fusible compounds with the lime. The melted alloy is either poured into water to granulate it, or cast in a very shallow mould of gas-charcoal.

Another method proposed by Deville and Debray is to treat the platinum ore with nitromuriatic acid, decant the liquid from the insoluble osmide of iridium, and slowly evaporate the solution of chloride of platinum, palladium, &c., till the residue begins to decompose. The red powder thus obtained is then heated to redness in a large covered crucible of earthenware or platinum provided with a neck to convey the gases into a chimney. When the calcination is finished, the platinum-powder is transferred to a wooden bowl, and washed in the same manner as auriferous earth or platinum ore itself. The dense shining platinum-powder which remains is then refined by fusion in the lime furnace as above. (Ann. Ch. Phys. [3] lvi. 385; Jahresb. 1859, p. 252.)

*Properties.*—Pure platinum when forged, and especially when refined by Deville and Debray's process, is nearly as white as silver; it takes a high lustre by polishing; has neither taste nor smell; and is very ductile and malleable. A platinum wire 2 millimetres in diameter, breaks with a weight of 124 kilogrammes. Platinum is softer than silver, but its hardness is much increased by the presence of traces of iridium; perfectly pure platinum is about as hard as copper. It expands by heat less than any other metal, and in its power of conducting heat and electricity, it is much inferior to gold and silver, and very near to iron (ii. 467; iii. 936). Platinum resists the strongest heat of a forge-fire, but may be fused by the electric current, or by the oxyhydrogen blowpipe, before which it is volatilised and dispersed with scintillations. According to Deville and Debray, it absorbs oxygen in the fused state, and if melted in considerable masses, spits like silver on rapid cooling. It has not been crystallised artificially, but very perfect octahedrons and cubes have been found in the native beds.

Platinum is the heaviest of all known substances, except osmium and iridium, which are equally dense. Its specific gravity varies according to the manner in which it has been treated; that of hammered platinum is 21·25; of platinum drawn into thick wire, 21·4; and after drawing into very thin wire, 21·5 (Wollaston); platinum solidified from fusion has a density of 21·15. (Deville and Debray.)

Platinum possesses a remarkable power of causing the combination of oxygen with hydrogen and other combustible gases (see COMBUSTION, i. 1092, and CONTACT-ACTION, ii. 12). This property is exhibited even by a clean surface of platinum, in a greater degree by platinum in the spongy state (p. 662), and most of all by the extremely divided form of the metal called platinum-black. The metal may be obtained in this form:—1. By dissolving platinous chloride in a hot and concentrated solution of potash, and pouring alcohol into it while still hot, by small quantities at a time; violent effervescence then occurs from the escape of carbonic anhydride, by which the contents of the vessel, unless capacious, may be thrown out. The liquor is decanted from the black powder which appears, and the latter boiled successively with alcohol, hydrochloric acid and potash, and finally four or five times with water, to divest it of all foreign matters.—2. By decomposing a hot solution of platinic sulphate with alcohol.—3. By boiling a solution of platinic chloride with carbonate of sodium and sugar: chloride of sodium is then formed, water and carbonic anhydride are produced by oxidation of the sugar, and the platinum is precipitated in the finely-divided state. —4. By precipitating the metal with zinc from a solution of platinic chloride containing excess of hydrochloric acid, or, according to Brunner, by digesting metallic zinc with a mixture of chloroplatinate of ammonium or potassium and strong sulphuric acid.—Platinum-black, when dried, resembles lamp-black, and soils the fingers, but still it is only metallic platinum extremely divided, and may be heated to full redness without any change of appearance or properties. It loses these properties, however, by the effect of a white heat, and assumes a metallic aspect. Platinum-black, like wood charcoal, absorbs and condenses gases, in its pores, with evolution of heat, a property which must assist its action on oxygen and hydrogen, although probably not essential to that action. When moistened with alcohol, it determines the oxidation of that substance in air, and the formation of acetic acid; and, in a similar manner, it converts wood-spirit into formic acid.

Platinum does not oxidise in the air at any temperature. It is not attacked by any single acid; but *nitromuriatic acid* dissolves it, though slowly. If heated to redness in the air in contact with *caustic alkalis* or *alkaline earths*, especially with hydrate of lithium or barium, it is corroded, in consequence of the formation of an oxide which unites with the alkali; it is also attacked at high temperatures by *acid sulphate of potassium*.

Spongy platinum unites with *sulphur* when the two are heated together somewhat strongly; hammered platinum is but very slowly attacked by sulphur. *Phosphorus* and *arsenic* easily unite with spongy platinum when heated with it, forming very fusible compounds. When an organic substance containing phosphorus—cerebral matter for example—is burnt in a platinum crucible, phosphorus is set free and unites with the platinum, forming a very fusible phosphide, so that the crucible sometimes becomes perforated. *Chlorine* is very slowly absorbed by platinum; *iodine* and *bromine* have no action upon it. A mixture of *silica* and charcoal easily attacks platinum at high temperatures by forming a silicide of platinum: hence platinum-crucibles must never be placed in direct contact with a coke or charcoal fire, but always enclosed in an earthen crucible containing magnesia.

*Uses.*—The unalterability of platinum at high temperatures, and its power of resisting the action of most chemical agents, render it extremely useful for the construction of crucibles, evaporating dishes, forceps for blowpipe experiments, &c. Large platinum stills, sometimes weighing more than 1000 ounces, are used for the concentration of oil of vitriol. They are gilt on the inner surfaces, because without this coating, platinum prepared by Wollaston's method soon becomes sufficiently porous to allow the transudation of the acid. An attempt was made in Russia to use platinum for coinage, but it was not found convenient. Platinum is sometimes used for the touch-holes of fowling-pieces. (*Miller's Elements of Chemistry*, ii. 828.)

*Compounds of Platinum.*—Platinum forms two series of compounds, the platinous compounds in which it is diatomic, *e.g.* $PtCl^2$, PtO, &c., and the platinic compounds in which it is tetratomic, *e.g.* $PtCl^4$, $PtO^2$, &c.[*] It shows but little tendency to form salts with oxygen-acids.

**PLATINUM, ALLOYS OF.** Platinum unites with most other metals, forming alloys which are for the most part more fusible than platinum itself: hence platinum crucibles must never be used for fusing other metals in, or even for igniting the oxides of the more fusible metals, such as lead and bismuth, whose oxides are easily reduced by contact with carbonaceous matter.

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[*] According to the older atomic weight of platinum, 98·7, adopted in the earlier part of this work (i. 465), the metal was regarded as monatomic in the platinous, and diatomic in the platinic compounds.

1 pt. of spongy platinum unites easily with 2 pts. of pulverised *antimony*, the combination being attended with vivid incandescence; and when the temperature is further raised, the compound fuses into a steel-grey, brittle, fine-grained alloy (Gehlen). Vivid incandescence is likewise produced by wrapping antimony in thin platinum-foil, and heating it before the blowpipe (Murray, Edinb. Phil. J. iv. 202). The alloy when heated in the air, gives up its antimony almost wholly, and leaves malleable platinum. (Fox, Ann. Phil. xiii. 467.)

100 pts. of spongy platinum heated with excess of *arsenic*, yield 173·5 pts. of arsenide of platinum, the combination being attended with vivid combustion. When platinum is heated with arsenious oxide and carbonate of sodium, arsenide of platinum and asenate of sodium are formed. Arsenic wrapped up in platinum-foil, likewise exhibits vivid combustion before the blowpipe (Murray). The alloy is brittle, and easily fusible. When it is heated in the air for some time, at a continually increasing temperature, but not sufficient to melt it, the arsenic gradually burns away, and leaves a porous residue of platinum in a state fit for working.

Platinum heated with an equal weight of *barium* before the oxy-hydrogen blowpipe melts to a bronze-coloured alloy, which in the course of 24 hours, decomposes and leaves a reddish powder. (Clarke, Gilb. Ann. lxii. 372.)

1 pt. of spongy platinum and 2 pts. of *bismuth* heated together combine readily, but without visible combustion, and form a bluish-grey, brittle, easily fusible alloy, having a laminated fracture (Gehlen). When this alloy is fused at a moderate heat, the two metals separate partially, according to their densities. When it is strongly ignited in contact with air, the greater part of the bismuth burns and forms a vitreous oxide, till the residue is no longer fusible.

Platinum heated with *cadmium* till the excess of the latter is volatilised, forms a silver-white, very brittle, fine-grained alloy, refractory in the fire and containing 46·02 per cent. platinum and 54·68 cadmium, therefore nearly $PtCd^2$. (Stromeyer.)

With *copper*, platinum does not combine below a white heat. Equal weights of platinum and copper, heated together in the oxy-hydrogen blowpipe flame, yield a pale yellow alloy having the colour and specific gravity of gold, extensible, easily attacked by the file, and tarnished by exposure to the air (Clarke). An alloy of 26 pts. copper and 1 platinum, is malleable, rose-coloured, and exhibits a fine-grained fracture. The alloys of copper and platinum take a fine polish and are sometimes used for the mirrors of telescopes.

7 pts. of platinum and 3 *gold* form an alloy infusible in the strongest blast-furnace. Alloys containing a larger proportion of gold fuse at that degree of heat (Prinsep). 2 pts. platinum and 1 gold form a brittle alloy. 1 pt. platinum and 1 gold form a very malleable alloy having nearly the same colour as gold. The alloy of 1 pt. platinum and 9·6 gold has the colour of gold and the density of platinum (Clarke). 1 pt. platinum and 11 gold form a greyish-white alloy, like tarnished silver. (Hatchett.)

The alloy of platinum and *iridium* has been already described (iii. 317); also the alloys of platinum, iridium and rhodium obtained by fusing platinum-ore (iv. 664).

The alloys of platinum and *iron* are described under IRON (iii. 369).

*Lead* unites very easily with platinum. Melted lead poured into a platinum-crucible dissolves a portion of the platinum. Lead wrapped in platinum-foil exhibits incandescence when heated (Murray). 1 pt. of spongy platinum and 2·7 of lead heated to redness together, combine without visible combustion, and form an easily fusible compound, which has the colour of bismuth, splits under the hammer, and exhibits a fibrous fracture. The alloy of 1 pt. platinum and 2 pts. lead is somewhat more brittle (Gehlen). An alloy containing equal quantities of the two metals has a purple colour and striated surface, and is hard, brittle, exhibits a granular fracture, and is altered by exposure to the air. When these alloys are heated to redness in the air, only part of the lead separates from the platinum, the separation going on indeed only so long as the alloy remains fusible.

The compounds of platinum and *mercury* have been already described (iii. 888).

Equal parts of platinum and *molybdenum* yield a hard, brittle, shapeless lump having a light grey colour and metallic lustre. 4 pts. platinum and 1 pt. molybdenum form a hard, brittle, bluish-grey alloy, having a granular fracture.

Equal parts of platinum and *nickel* placed upon a piece of charcoal burning in a stream of oxygen, unite quickly, and form a pale yellowish-white alloy, perfectly malleable, susceptible of a high polish, equal to copper in fusibility, and to nickel in magnetic power. (Lampadius.)

Equal parts of platinum and *palladium* unite somewhat below the melting-point of the latter, forming a grey alloy as hard as wrought iron, having a specific gravity of 15·141, less ductile than the alloy of palladium and gold. (Chenevix.)

With *potassium*, platinum unites readily, exhibiting incandescence and forming a shining, brittle alloy, which burns when heated in the air, and is decomposed by water, with formation of black scales, usually regarded as a hydride of platinum.

*Silver* unites with platinum in all proportions. A very small quantity of platinum renders silver hard. Hot oil of vitriol dissolves out the silver from the alloy, and leaves the platinum. Nitric acid always dissolves a certain quantity of platinum together with the silver, and with a certain proportion of silver the alloy is completely soluble in nitric acid.

The alloy of platinum and *sodium* resembles that of platinum and potassium.

*Tin* and platinum fused together in equal parts form a dark-coloured, hard, brittle, tolerably fusible alloy, having a coarse-grained structure. A very definite alloy of tin and platinum having the composition $Pt^2Sn^3$, is obtained by melting 1 pt. platinum with 10 pts. tin, leaving the mass to cool slowly and treating it with hydrochloric acid, which dissolves out the excess of tin, and leaves the alloy in beautiful geodes, lined with cubic crystals, or rhombohedrous having their angles very near to 90°. (Deville and Debray.)

*Zinc* appears also to form a definite alloy with platinum, analogous in composition to the preceding and obtained in like manner. (Deville and Debray.)

**PLATINUM, ANTIMONIDE OF.** (See p. 666.)

**PLATINUM, ARSENIDE OF.** (See p. 666.)

**PLATINUM, BORIDE OF.** Platinum heated with borax and charcoal, melts into a hard, brittle, somewhat crystalline mass, which when dissolved in nitromuriatic acid, leaves a residue of boric acid (Descotils, Ann. Chim. lxvii. 88). Boron heated on platinum-foil before the blowpipe immediately combines with the metal, forming a silver-white fusible compound. The same compound is likewise obtained by melting spongy platinum with boron under a layer of borax (Deville and Wöhler). Boride of platinum is easily pulverised; it is but slowly attacked by nitromuriatic acid. Its composition appears to be PtB. (Martius.)

**PLATINUM, BROMIDE OF.** The only bromide of platinum known is the *tetrabromide*, $PtBr^4$, which is a brown, deliquescent compound, obtained by dissolving platinum in a mixture of hydrobromic and nitric acids, and evaporating at a gentle heat. It unites with the more basic metallic bromides, forming double salts called bromoplatinates, having the composition $M^2PtBr^6 = 2MBr.Pt^{iv}Br^4$ and $M''PtBr^6 = M''Br^2.Pt^{iv}Br^4$. The *potassium-salt* separates from a mixture of the solutions of the component bromides, by spontaneous evaporation, in regular octahedrons and cubo-octahedrons of a red colour; it is sparingly soluble in water, insoluble in alcohol.—The *sodium-salt* prepared in a similar manner, crystallises in dark-red prisms, permanent in the air, easily soluble in water and in alcohol.—The *barium-*, *calcium-*, *magnesium-*, *manganese-*, and *zinc-salts* also crystallise in dark-red prisms. (Bonsdorff, Pogg. Ann. xix. 344; xxxiii. 61.)

**PLATINUM, CARBIDE OF.** This compound is obtained by boiling platinic chloride with tartaric acid, or by calcining certain organic platinum-salts at a moderate heat. It is black, insoluble in water, decomposible by nitromuriatic acid, which dissolves the platinum and leaves the carbon.

**PLATINUM, CHLORIDES OF.** Platinum forms two chlorides, namely, a di- and a tetrachloride.

**Dichloride of Platinum** or **Platinous Chloride,** $PtCl^2$. (*Protochloride*, according to the older atomic weight of platinum.)—This compound is prepared by dissolving platinum in nitromuriatic acid, evaporating to dryness, and cautiously heating the residue in an oil-bath to 200°, till it becomes insoluble in water. It is a greenish-brown solid body, permanent in the air at ordinary temperatures, but blackening on the surface by long exposure to light. It is insoluble in *water*, *nitric acid*, and *sulphuric acid*, but dissolves completely in *hydrochloric acid*, as dichloride if protected from the air, as tetrachloride if the air has access to it. The solution of the pure dichloride has a dark brown colour, gives with *potash* a dark brown precipitate of platinous hydrate, and with *ammonia* a green crystalline precipitate of diammonio-platinous chloride, $N^2H^6Pt''Cl^2$, insoluble in cold water and in alcohol (see PLATINUM-BASES). Platinous chloride dissolves in caustic potash or soda, and alcohol added to the solution throws down the whole of the platinum as platinum-black (p. 664). It is completely resolved at a red heat into chlorine and platinum.

If the heating of the platinic chloride be discontinued before half the chlorine has been driven off, the residue dissolves in water, forming a dark brown solution supposed by Magnus to contain platinoso-platinic chloride. On evaporating this solution, platinous chloride separates as a brown precipitate more soluble in hydrochloric acid than the original green compound, and regarded by Berzelius as a peculiar modification.

**Chloroplatinites.**—Platinous chloride unites with the more basic metallic chlorides, forming double salts represented by the formula $\mathrm{M^2Pt''Cl^4 = 2MCl.Pt''Cl^2}$ and $\mathrm{M''Pt''Cl^4 = M''Cl^2.Pt''Cl^2}$.

*Chloroplatinite of ammonium*, $\mathrm{(NH^4)^2Pt''Cl^4}$, is produced by adding sal-ammoniac to a solution of platinous chloride in hydrochloric acid, and crystallises by evaporation in red four-sided prisms.

*Chloroplatinite of Barium*, $\mathrm{Ba''Pt''Cl^4.3H^2O}$, is obtained by saturating a solution of platinous chloride in hydrochloric acid with carbonate of barium, and crystallises by spontaneous evaporation in dark red four-sided prisms, easily soluble in water, sparingly in alcohol of 90 per cent. It appears to give off only 2 at. water at 100°. The solution mixed with ammonia deposits the green salt of Magnus (p. 674). (J. Lang, J. pr. Chem. lxxxvi. 126; Jahresh. 1863, p. 230.)

*Chloroplatinite of Lead*, $\mathrm{Pb''Pt''Cl^4}$, prepared like the silver-salt (*infra*) resembles the latter in appearance, is insoluble in cold water, and is decomposed by boiling water. (Lang.)

*Chloroplatinite of Potassium*, $\mathrm{K^2Pt''Cl^4}$, prepared like the ammonium-salt, also forms red four-sided prisms, moderately soluble in water, insoluble in alcohol.

*Chloroplatinite of Silver*, $\mathrm{Ag^2Pt''Cl^4}$, separates on mixing a solution of the potassium-salt with nitrate of silver, as a light red precipitate. It is insoluble in water, blackens when exposed to light, and gives up all its platinum to warm hydrochloric acid. Ammonia first dissolves out the chloride of silver, and leaves a yellow substance which gradually dissolves in a large quantity of ammonia, forming a colourless solution which when left to evaporate, deposits a yellow powder and colourless prisms. (Lang.)

The *sodium-salt*, $\mathrm{Na^2Pt''Cl^4}$, is soluble in water and in alcohol, and difficult to crystallise.

*Stannous chloroplatinites.*—Platinous chloride forms with stannous chloride two double salts, which are obtained by dissolving stannous chloride in a solution of platinous chloride in hydrochloric acid, and evaporating, the one or the other being formed according to the proportions in which the salts are mixed. That which contains the smaller proportion of stannous chloride is a crystalline, olive-green, deliquescent, saline mass; that containing the larger proportion of stannous chloride is red; both are slightly soluble in water, and are decomposed by dilution with water. (Kane.)

*Chloroplatinite of Zinc*, $\mathrm{Zn''Pt''Cl^4}$, is formed, according to Hünefeld, when zinc is immersed in an aqueous solution of platinic chloride. It forms small, hard, shining, yellow crystals, sparingly soluble in cold, more soluble in boiling water, and precipitated by alcohol.

**Tetrachloride of Platinum or Platinic Chloride,** $\mathrm{Pt^{iv}Cl^4}$. (*Dichloride*, according to the old atomic weight of platinum.)—This compound is obtained by dissolving platinum in nitromuriatic acid and evaporating the solution over the water-bath. It then remains as a brown-red mass, which, if pure, dissolves in water and in alcohol with reddish-yellow colour; generally however it is red, owing to the presence of a small quantity of iridium. If more strongly heated, it gives off chlorine and leaves first platinous chloride and then metallic platinum.

The solution of platinic chloride gives with *potash*, *ammonia*, and their salts, a yellow crystalline precipitate of chloroplatinate of potassium or ammonium, sparingly soluble in water, insoluble in alcohol. When, however, dilute aqueous ammonia is added in excess to an aqueous solution of platinic chloride too dilute to yield a precipitate of the chloroplatinate, a pale yellow powder is precipitated after a while, consisting of $\mathrm{N^2H^6Pt^{iv}Cl^4}$ (see PLATINUM-BASES). Caustic *soda-solution* forms no precipitate in the cold, but on warming the solution a brownish-yellow precipitate is formed consisting of platinate of sodium.

*Sulphydric acid* produces in a solution of platinic chloride, at first only a brown coloration, afterwards a brown precipitate of platinic sulphide.

*Sulphide of ammonium* produces the same precipitate, but redissolves it when added in excess.—*Iodide of potassium* colours the solution brown-red, and precipitates brown platinic iodide.—*Stannous chloride* colours the solution brown-red.—*Mercuric nitrate* forms a copious reddish-yellow precipitate.—*Mercuric cyanide* forms no precipitate, thereby affording a distinction between platinum and palladium (p. 328). Platinum is not so easily reduced to the metallic state from its solutions as gold.—*Zinc* throws down metallic platinum; so likewise does *formic acid* on heating, if the free acid be neutralised with carbonate of sodium, but the reduction is not effected by *ferrous sulphate* or *oxalic acid*.

A compound of platinic chloride with *nitric oxide*, said to contain $\mathrm{5(PtCl^4.H^2Cl^2).4NO.10H^2O}$, is produced, according to Boye and Rodgers (Phil. Mag. Nov. 1840, p. 397), by mixing dry platinic chloride with a large excess of nitromuriatic acid: the liquid evaporated to a syrup deposits the compound as a yellow crystalline powder, which does not give off water at 100°, but in contact with water, is resolved, with effervescence, into its constituents.

**Chloroplatinates**, $M^2Pt^{iv}Cl^6 = 2MCl.Pt^{iv}Cl^4$ and $M''Pt^{iv}Cl^6 = M''Cl^2.Pt^{iv}Cl^4$. —Platinic chloride unites with other metallic chlorides, forming a class of well-defined double salts, among which the potassium- and ammonium-salts, on account of their sparing solubility in water and insolubility in alcohol, are of especial importance in analysis, affording the means of separating and estimating platinum on the one hand, and potassium and ammonium on the other.

*Chloroplatinate of Ammonium* or *Platinum-sal-ammoniac*, $(NH^4)^2Pt^{iv}Cl^6$, is precipitated as a heavy, lemon-yellow, crystalline powder on mixing a solution of platinic chloride with sal-ammoniac, and crystallises on cooling from a hot aqueous solution in regular octahedrons. When ignited it leaves metallic platinum in the spongy state. It is but slightly soluble in cold, more soluble in hot water; very slightly soluble in cold *water* containing ammonia, abundantly at the boiling heat (Fresenius, Ann. Ch. Pharm. lix. 118). A cold concentrated solution of sal-ammoniac precipitates it almost completely from its aqueous solution, but a hot solution of that salt dissolves it more abundantly than pure water, and the solution deposits a coating of platinum on copper and brass when they are boiled in it for a few seconds (Böttger). At 15°—20°, it dissolves in 26,535 pts. *alcohol* of 97·5 per cent.; in 1,406 pts. alcohol of 76 per cent., and in 665 pts. alcohol of 55 per cent.; but if free hydrochloric acid is present, the salt dissolves in 672 pts. alcohol of 76 per cent. at the same temperature (Fresenius). It dissolves easily, with decomposition, in a warm aqueous solution of *potassic sulphocyanate*. (Claus.)

*Chloroplatinate of Barium*, $Ba''Pt^{iv}Cl^6.4H^2O$, crystallises in orange-yellow prisms resembling chromate of lead (Bonsdorff, Pogg. Ann. xvii. 251).—The *cæsium-salt*, $Cs^2Pt^{iv}Cl^6$, has been already described (i. 1114).—The *calcium-salt*, $Ca''Pt^{iv}Cl^6.8H^2O$, crystallises with difficulty; when laid on bibulous paper it decomposes, chloride of calcium deliquescing out, and platinic chloride remaining.—The *cadmium-*, *cobalt-*, *copper-*, *magnesium-*, *manganese-*, *nickel-*, and *zinc-salts* are isomorphous, crystallise in rhombohedrons, and are all included in the general formula $M''Pt^{iv}Cl^6.6H^2O$.

*Chloroplatinate of Potassium*, $K^2Pt^{iv}Cl^6$, separates on mixing a solution of platinic chloride with chloride of potassium, in yellow crystalline grains having the form of the regular octahedron. It is not completely reduced by simple ignition, but when ignited with oxalic acid, or in a stream of hydrogen, it is completely resolved into chloride of potassium which may be dissolved out, chlorine which goes off as hydrochloric acid, and metallic platinum. The salt is sparingly soluble in *water*, insoluble or nearly so in *alcohol*. Its solubility in water at various temperatures, together with the solubilities of the corresponding cæsium- and rubidium-salts, as determined by Kirchhoff and Bunsen (Pogg. Ann. cxiii. 372), is given under CÆSIUM (i. 1114). It dissolves at 15°—20° in 12,083 pts. *alcohol* of 97·5 per cent, in 3,775 alcohol of 76 per cent., and in 1,053 pts. alcohol of 55 per cent.; but if a small quantity of free hydrochloric acid is present, it dissolves in 1,835 pts. alcohol of 76 per cent. (Fresenius, *loc. cit.*). It is slightly soluble in *acids*, dissolves with yellow colour in caustic *potash*, but is insoluble in alkaline carbonates. (H. Rose.)

*Chloroplatinate of Rubidium*, $Rb^2Pt^{iv}Cl^6$.—Platinic chloride forms in solutions of rubidium, especially at the boiling heat, a light yellow, heavy, pulverulent precipitate, which appears under the microscope to be composed of transparent, shining, regular octahedrons. It is quite insoluble in alcohol, and much less soluble in water than the potassium-salt. It is decomposed by hydrogen, partially even in the cold, and completely at a red heat, yielding a mixture of chloride of rubidium and metallic platinum. (Bunsen.)

*Chloroplatinate of Sodium*, $Na^2Pt^{iv}Cl^6.6H^2O$, crystallises in transparent, light yellow prisms easily soluble in water and in alcohol.

A compound of *platinic chloride* with *platinate of calcium*, $PtCl^4.\overset{\prime\prime}{Ca}{}^2Pt^{iv}O^4$, is produced, according to Döbereiner, by exposing the chloride mixed with milk of lime and a large quantity of lime-water to sunshine, as a white precipitate which turns yellowish on boiling.

**PLATINUM, CYANIDES OF.** (See CYANIDES, ii. 260.)

**PLATINUM, DETECTION AND ESTIMATION OF.**—1. *Blowpipe reactions.*—All platinum-compounds are reduced to spongy platinum in the inner flame; none of them give any colours to borax or microcosmic salt. The spongy platinum cannot be fused into a globule before the blowpipe.

2. *Reactions in Solution.*—Platinum almost always occurs in solution in the form of tetrachloride, the reactions of which have been already detailed. Solutions of platinic oxygen-salts, the sulphate and nitrate, for example, exhibit for the most part, the same reactions; with *potash* or *ammonia* however, they form a yellow-

brown precipitate, and with *chloride of potassium* or *ammonium*, a slight yellow precipitate of chloro-platinate after some time only.

Solutions of platinous salts, *e.g.* the sulphate and nitrate, and the double salts of platinous chloride, are distinguished from those of platinic salts by giving no precipitate with *sal-ammoniac* or with *potash*. With *carbonate of potassium* or *sodium* they form a brownish precipitate. *Ammonia* added to the solution of platinous chloride in hydrochloric acid throws down a green crystalline precipitate (p. 667); carbonate of ammonium forms no precipitate. With *sulphydric acid* and *sulphide of ammonium*, platinous solutions form a black precipitate soluble in excess of the ammonium-sulphide.

3. *Estimation and Separation.*—For quantitative estimation, platinum is usually precipitated from its solutions in the form of chloroplatinate of ammonium. The acid solution of platinum, after sufficient concentration, is mixed with a very strong solution of sal-ammoniac, and a sufficient quantity of strong alcohol is added to render the precipitation complete. The precipitate of chloroplatinate of ammonium is then washed with alcohol, to which a small quantity of sal-ammoniac has been added, and then heated to redness in a weighed porcelain crucible, whereupon it is decomposed and leaves metallic platinum. Great care must however be taken in the ignition to prevent loss, as the evolved vapours are very apt to carry away small particles of the salt and of the reduced metal. The best mode of avoiding this source of error is to place the precipitate in the crucible *enclosed in the filter*, and expose it for some time to a moderate heat, with the cover on the crucible, till the filter is charred, and then to a somewhat higher temperature to expel the chlorine and chloride of ammonium. The crucible is then partially opened and the carbonaceous matter of the filter burnt away in the usual manner. When these precautions are duly observed, not a particle of platinum is lost. Instead of igniting the the precipitate and weighing the platinum, the precipitate is sometimes collected on a weighed filter, dried over the water-bath and weighed; but this method is less accurate, because the precipitate always contains an excess of sal-ammoniac. (H. Rose.)

Chloride of potassium may also be used instead of chloride of ammonium to precipitate platinum, the concentrated solution of the platinum being previously mixed with a sufficient quantity of strong alcohol to bring the percentage of alcohol in the liquid to between 60 and 70 per cent. The precipitated chloro-platinate of potassium is then washed with alcohol of 60 to 70 per cent. and decomposed by simple ignition in a porcelain crucible, if its quantity is small, or in an atmosphere of hydrogen if its quantity is larger; the chloride of potassium is washed out by water; and the platinum dried, ignited, and weighed.

The same methods of precipitation serve also for the separation of platinum from most other metals, from all indeed excepting silver, lead, and mercurosum, which form insoluble or sparingly soluble chlorides, and from the other metals of the platinum group.

From mercury (in mercurous solutions) and from silver, platinum is easily separated by precipitating the mercury or silver with hydrochloric acid; from lead by precipitation with sulphuric acid. To separate platinum from silver, when the two metals are combined in an alloy, the best method is to heat the alloy with pure and strong *sulphuric acid*, diluted with about half its weight of water, till the sulphuric acid begins to escape in dense fumes. The silver is thereby converted into sulphate, and the platinum remains behind in the metallic state. The sulphate of silver is dissolved by a large quantity of hot water, the platinum washed with hot water, and again treated with sulphuric acid, to separate the last traces of silver.

From iridium, platinum is separated by precipitating the two metals together with sal-ammoniac, and reducing the chloro-iridiate of ammonium to soluble chloriridite by the action of sulphurous acid or other reducing agents (iii. 319, 320); from osmium, by volatilising the latter as osmic tetroxide (p. 244); from palladium, by precipitating that metal as cyanide (p. 328). For the method of separating it from rhodium and ruthenium, see those metals; also PLATINUM-ORE.

4. *Atomic Weight of Platinum.*—Berzelius (*Lehrbuch*, 5 Aufl. iii. 1213) found that 6·981 grms. chloroplatinate of potassium, $2KCl.PtCl^4$, lost by ignition 2·024 grms. chlorine, and left a mixture of 2·822 grms. platinum and 2·135 grms. chloride of potassium; hence,

$$\mathrm{Pt} = \frac{2{\cdot}822}{2{\cdot}135}\,2\mathrm{KCl} = \frac{2{\cdot}822}{2{\cdot}135}\,.\,149{\cdot}2 = 197{\cdot}7.$$

**PLATINUM, FLUORIDE OF.** *Platinic Fluoride*, $PtF^4$, is obtained, according to Berzelius, by dropping a solution of potassium-fluoride into a neutral aqueous solution of platinic chloride, as long as a precipitate of chloroplatinate of potassium continues to form, evaporating the filtrate to dryness, dissolving out the platinic fluoride by alcohol, adding water, and again evaporating at a heat below 60°. The fluoride then remains as a non-crystalline, yellow, transparent mass, perfectly soluble in water. At a higher temperature, it becomes dark brown, and when digested in water leaves a brown basic salt. It forms double salts with the fluorides of the alkali-metals.

**PLATINUM, IODIDES OF.** *Platinous iodide*, $PtI^2$, and *Platinic iodide*, $PtI^4$, are black, amorphous compounds obtained by precipitating the corresponding chlorides with iodide of potassium. Both are soluble in hydriodic acid.

Platinic iodide unites with the more basic metallic iodides, forming brown or black crystallisable compounds, $M^2Pt^{iv}I^6 = 2MI.Pt^{iv}I^4$, which yield dark red solutions.—The *ammonium-salt* crystallises in square tablets; the *potassium-salt* in black, rectangular tablets with four-sided pyramids attached; the *sodium-salt* in lead-grey, striated, deliquescent needles.

**PLATINUM, NITRIDE OF.** $Pt^3N^2$.—Obtained by heating the compound $4NH^3.Pt''H^2O^2$ (Reiset's base), to 180°. It decomposes suddenly at 190°, with evolution of nitrogen.

**PLATINUM, OXIDES OF.** Platinum forms two oxides corresponding to the chlorides, namely, $Pt''O$ and $Pt^{iv}O^2$, both of which are salifiable bases. According to E. Davy, there is also an oxide of intermediate composition.

**Platinous Oxide** is obtained as a hydrate, $Pt''O.H^2O$ or $Pt''H^2O^2$, by digesting platinous chloride in a warm solution of potash and washing the precipitate. Part of the platinous hydrate however remains dissolved in the alkali and may be precipitated by neutralising the liquid with sulphuric acid. The hydrate is a bulky black powder, easily decomposed by heat, giving off first water and afterwards oxygen. According to Berzelius, it may be converted by a very gentle heat into anhydrous platinous oxide, $Pt''O$. It dissolves slowly in acids, forming unstable salts, the reactions of which have already been described (p. 670). By boiling hydrochloric acid it is resolved into aqueous platinic chloride and metallic platinum. When recently precipitated it dissolves in *potash* and in *soda*, forming salts called platinites, which appear also to be formed when metallic platinum is heated with caustic alkalis (p. 665).

Platinous oxide forms with ammonia the two compounds $2NH^3.PtO$ and $4NH^3.PtO.H^2O$, which however are not produced by direct combination. (See PLATINUM-BASES.)

**Platinic Oxide,** $Pt^{iv}O^2$.—This oxide is somewhat difficult to obtain in the pure state. —1. From most platinum-salts alkalis throw down basic double salts; but from platinic nitrate, potash throws down at first the pure hydrate, which may be separated, and afterwards the double salt (Berzelius).—2. The hydrate may also be obtained by precipitating a hot solution of platinic sulphate with carbonate of calcium, dissolving out the excess of that substance from the precipitate by means of acetic acid, and then washing it for a long time [to remove the gypsum] (Wittstein).—3. Döbereiner mixes platinic chloride with excess of sodic carbonate, evaporates to dryness, heats the mixture gently, and dissolves out the chloride and excess of carbonate of sodium with water. There then remains a platinate of sodium containing $Na^2O.3PtO^2.6H^2O$, from which nitric acid removes the soda without dissolving the platinic oxide.

The hydrate (1) when recently precipitated, has a rusty colour, like that of hydrated ferric oxide; in drying, it shrinks together into a yellowish-brown mass. When heated, it gives off water, and turns black (Berzelius).—(2) is an umber-brown powder which does not decompose at 100°, but at a stronger heat, is resolved, with explosion and scattering of part of the mass in the form of a blackish fume, into aqueous vapour, oxygen gas, and platinum (Wittstein). When gently heated it is converted into the anhydrous oxide, $PtO^2$, which is a black powder.

A blue platinic oxide is formed, according to Hittorf, when platinum dipping into fused nitrate of potassium is made to form the negative pole of a voltaic circuit; it then flows continually from the platinum in the form of a blue liquid which afterwards changes into yellow and green oxide. In nitrate of sodium, the oxidation is weaker and the blue colour lighter and finer, the blue oxide thus formed changing its colour only to yellowish-brown.

Platinic hydrate dissolves in acids. The solutions yield on evaporation uncrystallisable platinic salts, the reactions of which have been already described (p. 669). They may also be obtained by decomposing a solution of platinic chloride with the potassium-salt of the required acid. Chloroplatinate of potassium is then precipitated, and another platinic salt (sulphate, nitrate, &c.) remains in solution.

Platinic oxide unites with strong bases, forming salts which may be called platinates. They are obtained by heating the corresponding chloroplatinates with excess of the alkali.

*Platinate of barium* is precipitated, according to Berzelius, as a light yellow powder, when a platinic salt is supersaturated with baryta; it is resolved at a red heat into platinum and baryta.—*Platinate of calcium* is obtained, according to Herschel, by exposing a mixture of platinic chloride and excess of lime-water to sunshine; but, according to Döbereiner, the precipitate thus formed likewise contains chlorine (p. 669).—*Platinate of potassium* is prepared by mixing chloroplatinate of potassium with an excess of potassic hydrate, moistening the mass with water, gradually heating it to dull redness and removing the excess of alkali by washing with water. It has a rust-brown colour; dissolves slowly in hydrochloric acid, not in nitric or sulphuric acid; is resolved by heat into platinous oxide and potash; and detonates violently with combustible bodies (Berzelius).—*Platinate of sodium* is obtained by exposing a mixture of aqueous platinic chloride and carbonate of sodium to sunshine, as a reddish-yellow, partly crystalline precipitate, $Na^2O.3PtO^2.6H^2O$, which when heated to redness, first gives off water, then oxygen, and leaves a black residue from which the soda may be dissolved out by water. It is decomposed by acids, which dissolve out the soda and leave the platinic oxide. (Weiss and Döbereiner, Ann. Ch. Pharm. xiv. 26.)

Respecting the compounds of platinic oxide with *ammonia*, see PLATINUM-BASES.

**PLATINUM, OXYGEN-SALTS OF.** The oxides of platinum dissolve in oxygen-acids, but the resulting salts have but little stability. Platinous nitrite and sulphite however unite with the sulphites of the more basic metals, forming crystallisable double salts.

*Platinous Nitrites.*—A solution of chloroplatinate of potassium mixed with nitrite of potassium, gradually deposits potassio-platinous nitrite, $K^2Pt''(NO^2)^4$, in colourless, six-sided prisms, which are permanent in the air, sparingly soluble in the mother-liquor, dissolve in 27 pts. water at 15°, in a smaller quantity of warm water, and separate from the solution unaltered. By slow evaporation of a more dilute solution, efflorescent rhombic prisms of a hydrated salt, $K^2Pt''(NO^2)^4.2H^2O$ are obtained.

The corresponding sodium-salt is very soluble in water and can be obtained in the crystalline state only by evaporation in vacuo. A hot saturated solution of the potassium-salt mixed with nitrate of silver, deposits the argento-platinous salt, $Ag^2Pt''(NO^2)^4$, in faintly yellowish tablets which blacken quickly when exposed to light. This salt decomposed by chloride of ammonium yields the ammonium-salt, $(NH^4)^2Pt''(NO^2)^4$, which by evaporation in a vacuum is obtained in pale yellow prisms permanent in the air; its solution gives off nitrogen when boiled. Mercuroso-platinous nitrite, $Hg^2Pt''(NO^2)^4.H^2O$, is obtained as a yellowish-white precipitate by decomposing the potassium-salt with a dilute slightly acid solution of mercurous nitrate. Baryto-platinous nitrate, $Ba''Pt''(NO^2)^4.3H^2O$, is obtained by decomposing the silver-salt with chloride of barium, and evaporating the filtrate at a gentle heat, in colourless octahedral crystals, slightly soluble in cold water. By decomposing the solution of this salt with an exactly equivalent quantity of sulphuric acid, and evaporating the filtrate in a vacuum, hydro-platinous nitrate or acid platinous nitrite, $H^2Pt''(NO^2)^4$, is obtained as a red saline mass, composed of indistinct prismatic crystals. Neutral platinous nitrite is not known. (J. Lang, J. pr. Chem. lxxxiii. 415; Rép. Chim. pure, iv. 220; Jahresb. 1861, p. 317.)

*Platinous sulphite* and its double salts will be described under SULPHITES.

**PLATINUM, PHOSPHIDE OF.** Platinum combines readily with phosphorus, becoming brittle and fusible. Phosphide of platinum is silver-white, hard, has a crystalline fracture, and is more fusible than silver. Schrötter, by heating spongy platinum in an atmosphere of phosphorus-vapour, has obtained a phosphide of platinum containing $PtP^2$, having a density of 8·77.

**PLATINUM, SELENIDE OF.** Spongy platinum heated with pulverised selenium forms a greyish infusible selenide.

**PLATINUM, SILICIDE OF.** When a mixture of platinum and charcoal-powder is exposed in a hessian crucible to the heat of a forge-fire, the silica in the crucible is reduced by the charcoal, and the liberated silicium unites with the platinum, forming a brittle compound which has a granular fracture; it dissolves very slowly in nitromuriatic acid, because it becomes covered with a layer of silicium which opposes the further action of the acid. (Boussingault, Ann. Ch. Phys. [2] xvi. 5.)

Silicium heated in a platinum crucible causes the metal to fuse on the surface, and imparts to it a crystalline texture. If the heat be raised to whiteness, the platinum becomes friable. Silicide of platinum containing 10 per cent. silicium, is hard, brittle, and fusible at a white heat.

By fusing platinum with excess of silicium in presence of cryolite, a white compound, $PtSi^6$, is formed having a grey, crystalline fracture. (Winckler, *Traité de Chimie par Pelouze et Frémy*, 3^me^. ed. iii. 1268.)

**PLATINUM, SILICOFLUORIDE OF.** The yellow solution of platinic oxide in hydrofluosilicic acid, dries up to a yellowish-brown gum, which when redissolved in water, leaves a brown basic salt. (Berzelius.)

**PLATINUM, SULPHIDES OF.** Two sulphides of platinum are known, analogous in composition to the oxides.

*Platinous Sulphide*, $Pt''S$, is obtained by decomposing platinous chloride with sulphydric acid or an alkaline sulphide, or by heating 2 pts. of sulphur with 1 pt. of finely divided platinum or 2 pts. of chloroplatinate of ammonium. It is a black substance, permanent in the air, insoluble in water, scarcely attacked by mineral acids even with aid of heat. When it is heated in contact with the air, the sulphur burns away and the platinum remains. According to Böttger, it acts upon alcohol in contact with the air like platinum-black, though much less rapidly.

*Platinic Sulphide*, $Pt^{iv}S^2$, is prepared:—1. By dropping aqueous platinic chloride into the solution of an alkaline sulphydrate, or by passing sulphydric gas through a solution of sodic chloroplatinate. (The precipitate formed by sulphydric acid in a solution of platinic chloride detonates partially when heated.)—2. By digesting 1 pt. of platinic chloride for several days with 4 pts. alcohol and 1 pt. sulphide of carbon. The mixture then concretes into a black mass, which when washed with alcohol and boiled several times with water, leaves platinic sulphide to be dried in a vacuum.

Platinic sulphide is black. When heated in a closed vessel, it gives off half its sulphur and is converted into platinous sulphide. When it is exposed to moist air, part of its sulphur is quickly oxidised to sulphuric acid. Hot nitric acid converts it into platinic sulphite.

Platinic sulphide dissolves in alkaline hydrates, carbonates and sulphides, forming salts called *sulphoplatinates*, which are decomposed by acids.

**PLATINUM, SULPHOCYANATES OF.** See SULPHOCYANATES.

**PLATINUM-BASES, AMMONIACAL.** (Reiset, Compt. rend. x. 870; xi. 711; xviii. 1100.—Gros, Ann. Ch. Pharm. xxvii. 241.—Peyrone, *ibid.* li. 1; lv. 205; lxi. 178.—Raewsky, *ibid.* lxiv. 309; lxviii. 316.—Gerhardt, Compt. chim. 1849, p. 273; Ann. Ch. Pharm. lxxvi. 307.—Gm. xvi. 296 *et seq.*)—The chlorides, oxides, sulphates &c. of platinum are capable of taking up ammonia, and forming compounds which may be represented as hydoramines $\left.\begin{matrix}mH^3N\\ nH^2O\end{matrix}\right\}$, hydrochloramines $\left.\begin{matrix}mH^3N\\ nHCl\end{matrix}\right\}$ &c., similarly to the ammoniacal compounds of mercury (iii. 921). In this manner are formed the five series of compounds formulated in the following table, in which R denotes a monatomic chlorous radicle:

| | | | |
|---|---|---|---|
| 1. Diammonio-platinous compounds . . . . | $\left.\begin{matrix}2H^3N\\ Pt''R^2\end{matrix}\right\}$ | = | $\left.\begin{matrix}H^6\\ Pt''\end{matrix}\right\}\begin{matrix}N^2\\ R^2\end{matrix}$ |
| 2. Tetrammonio-platinous compounds . . . . | $\left.\begin{matrix}4H^3N\\ Pt''R^2\end{matrix}\right\}$ | = | $\left.\begin{matrix}H^{12}\\ Pt''\end{matrix}\right\}\begin{matrix}N^4\\ R^2\end{matrix}$ |
| 3. Diammonio-platinic compounds . . . . | $\left.\begin{matrix}2H^3N\\ Pt^{iv}R^4\end{matrix}\right\}$ | = | $\left.\begin{matrix}H^6\\ Pt^{iv}\end{matrix}\right\}\begin{matrix}N^2\\ R^4\end{matrix}$ |
| 4. Tetrammonio-platinic compounds . . . . | $\left.\begin{matrix}4H^3N\\ Pt^{iv}R^4\end{matrix}\right\}$ | | |
| 5. Octammonio-diplatinic compounds . . . . | $\left.\begin{matrix}8H^3N\\ \overset{iv}{Pt^2}\left\{\begin{matrix}O''\\ R^6\end{matrix}\right.\end{matrix}\right\}$ | = | $\begin{matrix}H^{24}\\ \overset{iv}{Pt^2}\end{matrix}\left\{\begin{matrix}N^8\\ O''\end{matrix}\right.$ |

Any number of atoms of the monatomic radicle R may be replaced by an equivalent quantity of another radicle, mono- or polyatomic, thus giving rise to oxychlorides, nitrato-chlorides, oxalonitrates, &c.

1. *Diammonio-platinous Compounds.*—These compounds are formed by the action of heat on those of the following series, half the ammonia of the latter being then given off. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the tetrammonio-platinous compounds: they detonate when heated.

*Chloride*, $\left.\begin{matrix}H^6\\ Pt''\end{matrix}\right\}\begin{matrix}N^2\\ Cl^2\end{matrix}$—Of this compound there are three isomeric modifications:

*a. Yellow*, obtained by adding hydrochloric acid, or a soluble chloride, to a solution of diammonio-platinous nitrate or sulphate, or by boiling the green modification, γ, with nitrate or sulphate of ammonium, whereupon it dissolves and forms a solution which, on cooling, deposits the yellow salt;—or, by neutralising a solution of platinous chloride in hydrochloric acid with carbonate of ammonium, heating the mixture to the boiling point, and adding a quantity of ammonia equal to that already contained in the liquid, filtering from a dingy green substance, which deposits after a while, then leaving the solution to cool, and decanting the supernatant liquid as soon as the yellow salt is deposited. *β. Red.*—If, in the last mode of preparation, the carbonate of ammonium, instead of being added at once in excess, be added drop by drop to the hydrochloric acid solution of platinous chloride, the liquid on cooling deposits small garnet-coloured crystals having the form of six-sided tables. This red modification may also be obtained in other ways (Peyrone). *γ. Green.*—This modification, usually denominated the *green salt of Magnus*, was the first discovered of the ammoniacal platinum compounds. It is obtained by gradually adding an acid solution of platinous chloride to caustic ammonia; or by passing sulphurous acid gas into a boiling solution of platinic chloride, till it is completely converted into platinous chloride (and therefore no longer gives a precipitate with sal-ammoniac) and neutralising the solution with ammonia; the compound is then deposited in green needles. The same modification of the salt may also be obtained by adding an acid solution of platinous chloride to a solution of tetrammonio-platinous chloride, $N^4H^{12}Pt''Cl^2$. Hence it would appear that the true formula of this green salt is $N^4H^{12}\overset{\prime\prime}{Pt}{}^2Cl^4 = Pt''Cl^2.N^2H^6Pt''Cl^2$, that of the yellow or red modification being simply $N^2H^6Pt''Cl^2$. Either modification of the salt, when heated to 300°, gives off nitrogen, hydrochloric acid, and sal-ammoniac, and leaves a residue of platinum.

Platinous chloride forms similar compounds with ethylamine and methylamine (p. 679).

A red crystalline compound of diammonio-platinous chloride with chloride of ammonium, viz., $N^2H^6PtCl^2.2NH^4Cl$, is formed when a solution of tetrammonio-platinous chloride containing a large quantity of sal-ammoniac, is evaporated to the crystallising point. Thus, when a solution of platinous chloride in hydrochloric acid is precipitated by ammonia, and the green salt of Magnus thereby formed is heated, while still in the liquid, with excess of ammonia, to convert it into tetrammonio-platinous chloride, this red compound separates at a certain degree of concentration, together with the tetrammonio-platinous chloride. (Grimm, Ann. Ch. Pharm. xcix. 95.)

***Cyanide***, $\begin{matrix}H^4\\Pt''\end{matrix}\Big\}\begin{matrix}N^2\\Cy^2\end{matrix}$.—Obtained by adding hydrocyanic acid to a solution of tetrammonio-platinous oxide, cyanide of ammonium being formed at the same time (Reiset):

$$N^4H^{12}Pt''O \ + \ 4HCy \ = \ N^2H^6Pt''Cy^2 \ + \ 2NH^4Cy \ + \ H^2O.$$

Also, by digesting ammonio-platinous chloride with cyanide of silver. It crystallises in fine regular needles of a pale yellow colour, soluble with tolerable facility in water and ammonia. A polymeric modification of this compound, $N^4H^{12}Pt^2Cy^4 = N^4H^{12}PtCy^2.PtCy^2$, is formed by passing cyanogen gas into a moderately concentrated solution of tetrammonio-platinous oxide; the cyanogen then decomposes the water, forming hydrocyanic and cyanic acids, and the hydrocyanic acid acts upon the tetrammonio-platinous oxide, forming the compound $N^4H^{12}Pt^2Cy^4$, together with ammonia and water:

$$2N^4H^{12}PtO \ + \ 4HCy \ = \ N^4H^{12}Pt^2Cy^4 \ + \ 4NH^3 \ + \ 2H^2O.$$

The compound $N^4H^{12}Pt^2Cy^4$ crystallises out and may be purified by recrystallisation from water. It is also obtained by mixing a solution of tetrammonio-platinous chloride with cyanide of potassium. It forms crystals which, under the microscope, appear like six-sided tables arranged in stellate groups; it dissolves without decomposition in potash, hydrochloric acid, and dilute sulphuric acid, but is decomposed by strong sulphuric and by nitric acid. (Buckton, Chem. Soc. Qu. J. iv. 34.)

***Iodide***, $\begin{matrix}H^4\\Pt''\end{matrix}\Big\}\begin{matrix}N^2\\I^2\end{matrix}$.—Yellow powder, obtained by boiling the aqueous solution of the the compound $N^4H^{12}Pt''I^2$. It dissolves in ammonia, and is thereby reconverted into the latter compound.

***Oxide***, $N^2H^6Pt''O = \begin{matrix}H^4\\Pt''\end{matrix}\Big\}\begin{matrix}N^2\\O''\end{matrix}$.—Obtained by heating tetrammonio-platinous hydrate to 110°. It is a greyish mass which, when heated to 200° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. Probably the compound $Pt^3N^2$, is first produced, and is afterwards resolved into nitrogen and platinum:

$$3N^2H^6PtO \ = \ Pt^3N^2 \ + \ 4NH^3 \ + \ 3H^2O.$$

The oxide, heated to 200° in contact with the air, becomes incandescent, and burns vividly, leaving a residue of platinum.

The *sulphate*, $\left.\begin{matrix}H^6\\Pt''\end{matrix}\right\}\begin{matrix}N^2\\SO^4\end{matrix}.H^2O$, and the *nitrate*, $\left.\begin{matrix}H^6\\Pt''\end{matrix}\right\}\begin{matrix}N^2\\(NO^3)^2\end{matrix}$ are obtained by boiling the iodide with sulphate and nitrate of silver: they are crystalline and have a strong acid reaction. The sulphate retains an atom of crystallisation-water, which cannot be removed without decomposing the salt.

### 2. *Tetrammonio-platinous Compounds.*

*Chloride*, $\left.\begin{matrix}H^{12}\\Pt''\end{matrix}\right\}\begin{matrix}N^4\\Cl^2\end{matrix}$.—This compound is prepared by boiling platinous chloride, or the green salt of Magnus, with aqueous ammonia till the whole is dissolved, and evaporating the liquid to the crystallising point. Or, by passing sulphurous acid gas into tetrachloride of platinum till the solution is completely decolorised, precipitating with carbonate of sodium, dissolving the precipitate of sodio-platinous sulphite in hydrochloric acid, saturating the resulting solution of chloride of sodium and platinous chloride with ammonia, and dissolving the precipitate of di- and tetrammonio-platinous chloride in boiling hydrochloric acid. The filtered liquid on cooling deposits the former, while the tetrammoniacal compound remains in solution and may be obtained by evaporation, mixed however with sal-ammoniac. It separates in bulky crystals of a faint yellow colour, containing 1 at. water, which is completely given off at 110°. At 250° it gives off ammonia, and leaves diammonio-platinous chloride. The anhydrous compound rapidly absorbs water from the air. The hydrate does not give off ammonia when treated with caustic alkalis in the cold, and is but very slowly decomposed by them, even with the aid of heat.

Ethylamine and methylamine form similar compounds with platinous chloride, (p. 679).

*Tetrammonio-platinous chloride* forms two compounds with tetrachloride of platinum. The first, whose formula is $2N^4H^{12}Pt''Cl^2.Pt^{iv}Cl^4$, is obtained as an olive-green precipitate on adding tetrachloride of platinum to a solution of tetrammonio-platinous chloride; the second, $N^4H^{12}Pt''Cl^2.Pt^{iv}Cl^4$, by treating the preceding with excess of tetrachloride of platinum.

*Tetrammonio-cuprico-platinous chloride*, $\left.\begin{matrix}H^{12}\\Cu''\\Pt''\end{matrix}\right\}\begin{matrix}N^4\\Cl^6\end{matrix}$ is produced on adding platinic chloride to a concentrated ammoniacal solution of cuprous chloride, as a violet or grey precipitate composed of prismatic crystals, insoluble in water and in alcohol, permanent when dry, slowly decomposed by water. (Millon and Commaille, Compt. rend. lvii. 822.)

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes.

*Oxide*, $\left.\begin{matrix}H^{12}\\Pt''\end{matrix}\right\}\begin{matrix}N^4\\O''\end{matrix}$.—Obtained by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in vacuo. A crystalline mass is then left, containing the oxide. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates oxide of silver from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 110°, giving off water and ammonia, and leaving diammonio-platinous oxide. Its aqueous solution does not give off ammonia, even when boiled.

*Carbonates.*—The oxide absorbs carbonic anhydirde rapidly from the air, forming first, a neutral carbonate, $N^4H^{12}Pt''CO^3.H^2O$, and afterwards an acid salt, $N^4H^{12}Pt''CO^3.H^2CO^3$.

The *sulphate*, $\left.\begin{matrix}H^{12}\\Pt''\end{matrix}\right\}\begin{matrix}N^4\\SO^4\end{matrix}$, and the *nitrate*, $\left.\begin{matrix}H^{12}\\Pt''\end{matrix}\right\}\begin{matrix}N^4\\(NO^3)^2\end{matrix}$, are obtained by decomposing the chloride with sulphate or nitrate of silver; they are neutral, and crystallise easily.

*Sulphites.*—The salt $\left.\begin{matrix}H^{24}\\\overset{''}{Pt}{}^2\end{matrix}\right\}\begin{matrix}N^8\\(\overset{''}{S}O^3)^4\end{matrix}$ is obtained by boiling the green salt of Magnus in water with an equal quantity of ammonium-sulphite, as a white powder, insoluble in alcohol and in cold water, very slightly soluble in boiling water. By prolonged ebullition with excess of ammonium-sulphite, a solution is formed from which alcohol throws down oily drops, uniting into a glutinous mass of variable composition; and the alcohol used for the precipitation deposits after a while small white flakes of another sulphite, $\left.\begin{matrix}H^6\\Pt''\end{matrix}\right\}\begin{matrix}N^6\\(SO^3)^3\end{matrix}$. (Peyrone, Ann. Ch. Pharm. lxi. 178; Gm. vi. 305.)

### 3. *Diammonio-platinic Compounds.*

The *chloride*, $\left.\begin{array}{r}H^6\\Pt^{iv}\end{array}\right\}\begin{array}{l}N^2\\Cl^4\end{array}$ is obtained by passing chlorine gas into boiling water in which diammonio-platinous chloride (the yellow modification, p. 674) is suspended. This compound is insoluble in cold water, and very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of tetrammoniacal platinic chloride. The compound $N^2H^6Pt^{iv}Cl^4$ dissolves in boiling potash without evolving ammonia. A polymeric compound,

$$N^4H^{12}\overset{iv}{Pt^2}Cl^8 = N^4H^{12}Pt^{iv}Cl^4.Pt^{iv}Cl^4,$$

is obtained by passing chlorine into water in which Magnus's green salt is suspended. A red crystalline powder is at first precipitated, consisting of $N^4H^{12}PtCl^2.PtCl^4$; but on continuing the passage of the chlorine, this precipitate redissolves, and the solution yields, by evaporation, the crystalline compound, $N^4H^{12}Pt^2Cl^8$.

*Nitrates.*—An *oxynitrate*, $\left.\begin{array}{r}H^6\\Pt^{iv}\end{array}\right\{\begin{array}{l}N^2\\(NO^3)^2\\O''\end{array}$, is obtained by boiling the chloride, $N^2H^6PtCl^4$, for several hours with a dilute solution of nitrate of silver. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The normal nitrate, $\left.\begin{array}{r}H^6\\Pt^{iv}\end{array}\right\}\begin{array}{l}N^2\\(NO^3)^4\end{array}$, is obtained by dissolving the oxynitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N^2H^6Pt^{iv}O^2 = \left.\begin{array}{r}H^6\\Pt^{iv}\end{array}\right\}\begin{array}{l}N^2\\O^2\end{array}$, is obtained by adding ammonia to a boiling solution of diammonio-platinic nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small shining rhomboïdal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallisable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water (Gerhardt, Compt. chim. 1849, p. 273). Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing chloroplatinate of ammonium with aqueous potash. It is a straw-coloured powder which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

The *oxy-oxalate*, $\left.\begin{array}{r}H^6\\Pt^{iv}\end{array}\right\{\begin{array}{l}N^2\\(C^2O^4)''\\O''\end{array}$, is formed by decomposing the nitrate with oxalate of ammonium. It is a light yellow precipitate, soluble in boiling water, and detonating when heated.

The *sulphate*, $\left.\begin{array}{c}H^6N^2\\Pt^{iv}(SO^4)^2\end{array}\right\}$, is obtained by dissolving the oxide in dilute sulphuric acid and evaporating. It is a yellow powder, having an acid taste, and soluble in boiling water.

### 4. *Tetrammonio-platinic Compounds.*

The oxide of this series has not yet been isolated.

*Chloride*, $\left.\begin{array}{r}H^{12}\\Pt^{iv}\end{array}\right\}\begin{array}{l}N^4\\Cl^4\end{array}$.—Obtained by passing chlorine gas into a solution of tetrammonio-platinous chloride; by dissolving diammonio-platinic chloride in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of tetrammonio-platinic oxynitrate or nitrato-chloride (p. 677) with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent, regular octahedrons, having a faint yellow tint. When a solution of this salt is treated with nitrate of silver, one half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt (Grimm). A compound having the formula $N^4H^{10}PtCl^2$, containing, therefore, 2 at. Cl and 2 at. H less than the preceding, is obtained by dissolving chloroplatinate of ammonium in ammonia, and precipitating by alcohol; but it does not crystallise, merely drying up to a pale yellow resinous mass: hence its composition is doubtful.

*Chlorobromide*, $H^{12}N^4Pt^{iv}Br^2Cl^2$.—Prepared by treating tetrammonio-platinous chloride with bromine.

*Nitrates.*—A basic *nitrate* or *oxynitrate*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{NO}^3)^2\\ \mathrm{O}''\end{matrix}$, is produced by boiling the nitrato-chloride *b* with ammonia. It is a white amorphous powder slightly soluble in cold, more soluble in boiling water.

*Nitrato-chloride*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{NO}^3)^2\\ \mathrm{Cl}^2\end{matrix}$.—This salt, discovered by Gros, is obtained by treating Magnus's green salt with strong nitric acid. The green compound first turns brown, and is afterwards converted into a mixture of platinum and a white powder, which is dissolved out by boiling water, and crystallises on cooling in shining, flattened, colourless or pale yellow prisms:

$$2\mathrm{N}^2\mathrm{H}^6\mathrm{PtCl}^2 + 2\mathrm{HNO}^3 = \mathrm{N}^4\mathrm{H}^{12}\mathrm{PtCl}^2(\mathrm{NO}^3)^2 + \mathrm{Pt} + 2\mathrm{HCl}.$$

This salt dissolves readily in water, especially when heated. The chlorine and platinum contained in the solution cannot be detected by the ordinary reagents; thus nitrate of silver and sulphydric acid yield but very trifling precipitates even after a long time.

*Oxalochloride*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{C}^2\mathrm{O}^4)''\\ \mathrm{Cl}^2\end{matrix}$.—Oxalic acid or an alkaline oxalate added to the solution of the corresponding sulphato-chloride or nitrato-chloride throws down this salt in the form of a white granular precipitate, insoluble in water.

*Oxalo-nitrate*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{C}^2\mathrm{O}^4)''\\ (\mathrm{NO}^3)^2\end{matrix}$.—Deposited as a white crystalline body from the solution of octammonio-diplatinic oxalo-nitrate in dilute nitric acid.

*Phosphato-chloride*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{PO}^4)'''\\ \mathrm{Cl}\end{matrix}.\tfrac{1}{2}\mathrm{H}^2\mathrm{O}$.—Obtained as a crystalline precipitate on mixing a warm concentrated solution of the nitrato-chloride with trisodic phosphate; from cold dilute solutions the salt crystallises, after a longer time, in radiate groups of small, white, strongly lustrous needles. It is nearly insoluble in cold, and only slightly soluble in boiling water. (Raowsky.)

*Sulphato-chloride*, $\left.\begin{matrix}\mathrm{H}^{12}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^4\\ (\mathrm{SO}^4)''\\ \mathrm{Cl}^2\end{matrix}$.—Obtained by treating tetrammonioplatinic chloride or nitrato-chloride with dilute sulphuric acid, or by mixing the solution of the nitrato-chloride with a strong solution of a soluble sulphate. It crystallises in slender needles, sparingly soluble in cold, moderately soluble in boiling water. The sulphuric acid in the solution is not precipitated by barium-salts. The sulphato-chloride is, however, decomposed by hydrochloric or nitric acid, either of which takes the place of the sulphuric acid, reproducing the chloride or nitrato-chloride. (Gros.)

### 5. *Octammonio-diplatinic Compounds.*

*Oxynitrate* or *Basic Nitrate*, $\left.\begin{matrix}\mathrm{H}^{24}\\ \mathrm{Pt}^{\mathrm{iv}}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^8\\ (\mathrm{NO}^3)^6\\ \mathrm{O}''\end{matrix}$.—This salt is produced by boiling diammonio-platinous oxynitrate (p. 675) with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid. (Gerbardt.)

*Nitrat-oxychloride*, $\left.\begin{matrix}\mathrm{H}^{24}\\ \mathrm{Pt}^{\mathrm{iv}}\\ \mathrm{Pt}^{\mathrm{iv}}\end{matrix}\right\}\begin{matrix}\mathrm{N}^8\\ (\mathrm{NO}^3)^4\\ \mathrm{O}''\\ \mathrm{Cl}^2\end{matrix}$.*—This salt, discovered by Raewsky, is formed when Magnus's green salt is boiled with a large excess of nitric acid. Red fumes are then evolved, and the resulting solution deposits the nitrat-oxychloride in small brilliant needles which deflagrate when heated, giving off water and sal-ammoniac and leaving metallic platinum.

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* Raewsky assigns to this salt the formula $8\mathrm{NH}^3.\mathrm{Pt}^2\mathrm{Cl}^2\mathrm{O}^5.2\mathrm{N}^2\mathrm{O}^5$, which contains 2 at. oxygen more than that above given, and corresponding formulæ to all the other salts of this series. Such formulæ, however, could not be reduced to any type similar to those by which the other ammoniacal platinum-compounds are represented, and moreover Raewsky's platinum-determinations appear to be all too low, having been made by a method which almost necessarily involves a loss of platinum. Gerhardt therefore proposed the formulæ above given.

The nitric acid in this salt may be replaced by an equivalent quantity of *carbonic* or *oxalic* acid, yielding the salts $\begin{matrix}H^{24}\\ Pt^{iv}\\ Pt^{iv}\end{matrix}\left\{\begin{matrix}N^{8}\\ (CO^{3})^{2}\\ O''\\ Cl^{2}\end{matrix}\right.$ and $\begin{matrix}H^{24}\\ Pt^{iv}\\ Pt^{iv}\end{matrix}\left\{\begin{matrix}N^{8}\\ (C^{2}O^{4})^{2}\\ O''\\ Cl^{2}\end{matrix}\right.$, both of which are sparingly soluble and easily crystallisable.

A *basic oxalonitrate*, $\begin{matrix}H^{24}\\ Pt^{iv}\\ Pt^{iv}\end{matrix}\left\{\begin{matrix}N^{8}\\ (C^{2}O^{4})^{2}\\ (NO^{3})^{2}\\ O''\end{matrix}\right.$, insoluble in water, is obtained by adding oxalate of ammonium to the oxynitrate. (Gerhardt.)

### *Theories of the Constitution of the Ammoniacal Platinum-compounds.*

*a*. These compounds may be formulated as salts of ammonium-bases, if it be admitted that the hydrogen in the ammonium-molecule may in some cases be partly replaced by ammonium itself, in others by the diatomic radicles, $Pt^{iv}Cl^{2}$ and $Pt^{iv}O$: thus, taking the chlorides for example:

| | | |
|---|---|---|
| $N^{2}H^{6}Pt''Cl^{2}$<br>Diammonio-platinous chloride. | = | $N^{2}(H^{6}Pt'').Cl^{2}$.<br>Chloride of Platoso-diammonium. |
| $N^{4}H^{12}Pt''Cl^{2}$<br>Tetrammonio-platinous chloride. | = | $N^{2}[H^{4}(NH^{4})^{2}Pt^{iv}].Cl^{2}$.<br>Chloride of Diammoplatoso-diammonium. |
| $N^{2}H^{6}Pt^{iv}Cl^{4}$<br>Diammonio-platinic chloride. | = | $N^{2}[H^{6}(Pt^{iv}Cl^{2})''].Cl^{2}$.<br>Chloride of Chloroplatoso-diammonium. |
| $N^{4}H^{12}Pt^{iv}Cl^{4}$<br>Tetrammonio-platinic chloride. | = | $N^{4}(H^{12}Pt^{iv}).Cl^{4}$.<br>Chloride of Platino-tetrammonium. |

In like manner, diammonio-platinic oxide, $N^{2}H^{6}Pt^{iv}O^{2}$, may be formulated as oxide of oxyplatosammonium, $N^{2}[H^{6}(Pt^{iv}O)''].O$; diammonio-platinic oxynitrate, $N^{2}H^{6}.Pt^{iv}\left\{\begin{matrix}(NO^{3})^{2}\\ O''\end{matrix}\right.$, as nitrate of oxyplatosodiammmonium, $N^{2}[H^{6}(Pt^{iv}O)''].(NO^{3})^{2}$; Raewsky's octammonio-diplatinic-nitratoxychloride, $N^{8}H^{24}.\overset{iv}{Pt^{2}}\left\{\begin{matrix}(NO^{3})^{4}\\ O''\\ Cl^{2}\end{matrix}\right.$, as nitrate of ammo-oxychloro-platino-tetrammonium, $N^{4}[H^{8}(NH^{4})^{4}(Pt^{iv}O)''(Pt^{iv}Cl^{2})''](NO^{3})^{4}$, &c., &c.

*β. Gerhardt's Theory*. Gerhardt regards the ammoniacal platinum-compounds as salts of ammonia-bases formed by the substitution of one or two equivalents of platinum for hydrogen in a single or double molecule of ammonia, $NH^{3}$, admitting, however, that platinum may enter its compounds with two different equivalent weights, namely as *platinosum* = 98·7 = Pt, and as *platinicum* = 49·35 = pt. This being admitted, the ammonio-platinous compounds may be regarded as salts of platosamine $NH^{2}Pt$ and of diplatosamine $N^{2}H^{5}Pt$, and the ammonio-platinic compounds as salts of platinamine $NHpt^{2}$ and of diplatinamine $N^{2}H^{4}pt^{2}$: thus

| | | |
|---|---|---|
| $\frac{1}{2}(N^{2}H^{6}Pt''Cl^{2})$<br>Diammonio-platinous chloride. | = | $NH^{2}Pt.HCl$.<br>Hydrochlorate of Platosamine. |
| $\frac{1}{2}(N^{4}H^{12}Pt''Cl^{2})$<br>Tetrammonio-platinous chloride. | = | $N^{2}H^{5}Pt.HCl$.<br>Hydrochlorate of Diplatosamine. |
| $\frac{1}{2}(N^{2}H^{6}Pt^{iv}Cl^{4})$<br>Diammonio-platinic chloride. | = | $NHpt^{2}.2HCl$.<br>Dihydrochlorate of Platinamine. |
| $\frac{1}{2}(N^{4}H^{12}Pt^{iv}Cl^{4})$<br>Tetrammonio-platinic chloride. | = | $N^{2}H^{4}pt^{2}.2HCl$.<br>Dihydrochlorate of Diplatinamine. |
| $\frac{1}{2}[N^{4}H^{12}.Pt^{iv}(NO^{3})^{2}Cl^{2}]$<br>Tetrammonio-platinic Nitrato-chloride. | = | $N^{2}H^{4}pt^{2}\left\{\begin{matrix}HCl\\ HNO^{3}\end{matrix}\right.$<br>Chlorhydro-nitrate of Diplatinamine. |
| $N^{8}H^{24}.\overset{iv}{Pt^{2}}(NO^{3})^{4}Cl^{2}O$<br>Octammonio-diplatinic nitratoxychloride. | = | $2\left[2N^{2}H^{4}pt^{2}\left\{\begin{matrix}HCl\\ 2HNO^{3}\end{matrix}\right.\right].H^{2}O$<br>Sesquichlorhydronitrate of Diplatinamine. |

These formulæ, however, as well as those based on the ammonium-type (p. 678), must be regarded merely as numerical expressions, and not by any means as representations of the rational constitution of the compounds.

**PLATINUM-BASES, ORGANIC.** Methylamine and ethylamine act readily at ordinary temperatures on platinous chloride suspended in water, forming compounds analogous in composition and properties to Magnus's green salt (p. 674). The *methylamine-salt*, $(CH^5N)^4Pt''Cl^4 = Pt''Cl^2.(CH^5N)^4Pt''Cl^2$, is a chrome-green powder; the *ethylamine-salt*, $(C^2H^7N)^4Pt''^2Cl^4$, is chamois-coloured; both are insoluble in water. The methylamine salt boiled in a sealed flask with excess of methylamine, gradually dissolves, leaving only a small quantity of a black detonating substance analogous to fulminating platinum (p. 676), and the solution evaporated to a syrup, ultimately solidifies to a crystalline mass of the salt $(CH^5N)^4Pt''Cl^2$, analogous to tetrammonio-platinous chloride (p. 675). The *ethylamine-salt* $(C^2H^7N)^4.Pt''Cl^2$, prepared in like manner, crystallises in splendid colourless prisms containing 2 at. water, moderately soluble in water, sparingly so in alcohol. This salt treated with sulphate of silver yields chloride of silver, and *tetrethylammonio-platinous sulphate* $(C^2H^7N)^4.Pt''(SO^4)$, in colourless crystals of considerable size. (Wurtz, Ann. Ch. Phys. [3] xxx. 443.)

*Chinoline* heated to boiling with platinous chloride forms a pale yellow powder, $(C^9H^7N)^2.Pt''Cl^2$, which is nearly insoluble in water, but dissolves in excess of chinoline, forming a solution from which acids throw down the yellow *hydrochlorate*, $(C^9H^7N)^2.Pt''Cl^2.2HCl$: this latter, when boiled with chinoline, is reconverted into the original substance. (Gr. Williams, Jahresb. 1858, p. 357.)

*Piperidine* forms under similar circumstances, and with energetic action, a yellow compound $(C^5H^{11}N)^2Pt''Cl^2$, soluble in a large quantity of boiling water. (Gr. Williams.)

**PLATINUM-BLACK.** See PLATINUM (p. 666).

**PLATINUM-ORE** or *Native Platinum.* This ore is usually found in auriferous alluvial sand or drift, in thin scales or irregular grains not exceeding the size of a small pea, occasionally however in larger masses or nuggets; one of these weighing 800 grammes was found in the gold mine of Condoto, Peru; and in the mines of Demidoff in the Ural, masses have been found weighing 6½, 9, and 9½ kilogrammes.

Platinum-ore is composed essentially of platinum, iridium, osmium, palladium, rhodium, ruthenium, iron, copper, and osmide of iridium, with which also are associated chrome-iron, titaniferous iron, small scales of alloys of gold and silver, small hyacinths, and small quantities of mercury and sand.

*Analyses:* *a.* From Giroblagodat in the Ural; non-magnetic: *α.* by Berzelius (Pogg. Ann. xiii. 435, 527, 553); *β.* by Claus, *Beiträge zur Geschichte der Platinmetalle*, Dorpat, 1854, p. 60).—*b.* From Nischne Tagilsk: *α.* by Osann (*Rammelsberg's Mineralchemie*, p. 11); *β.* Very dark grey; magnetic; *γ.* Dark grey, non-magnetic grains (Berzelius).—*c.* From Barbacon, Oregon: larger grains (Berzelius).—*d.* From the same locality (Claus).—*e.* From Borneo: small grains (after deduction of 3·8 per cent. osmide of iridium and 0·2 gold (Böcking, Ann. Ch. Pharm. xcvi. 243).—*f.* From the same: laminæ or flat grains (after deduction of 3·97 per cent. gold and 8·83 insoluble matter, containing osmide of iridium and 1·63 per cent. cupric and ferric oxides) (Bleckerode, Pogg. Ann. ciii. 656).

| | *a.* | | *b.* | | | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|---|---|---|
| | *α.* | *β.* | *α.* | *β.* | *γ.* | | | | |
| Platinum . . . | 86·50 | 85·97 | 83·07 | 78·94 | 73·58 | 84·30 | 84·80 | 86·10 | 82·05 |
| Rhodium . . . | 1·15 | 0·96 | 0·59 | 0·86 | 1·15 | 3·46 | 2·07 | . . | 0·59 |
| Iridium . . . | . . | 0·98 | 1·91 | 4·97 | 2·35 | 1·46 | 1·02 | 0·69 | 7·16 |
| Osmium* . . . | . . | 0·54 | . . | . . | . . | 1·03 | 1·01 | 0·31 | 1·34 |
| Palladium . . . | 1·10 | 0·75 | 0·26 | 0·28 | 0·30 | 1·06 | 1·00 | . . | 1·69 |
| Iron . . . . | 8·32 | 6·54 | 10·79 | 11·04 | 12·98 | 5·31 | 8·28 | 11·12 | 6·78 |
| Copper . . . | 0·45 | 0·86 | 1·30 | 0·70 | 5·20 | 0·74 | 0·64 | 0·14 | 0·39 |
| Admixtures, osmiridium &c. . | 1·40 | 2·10 | 1·80 | 1·96 | 2·30 | 0·72† | | | |
| | 98·92 | 98·70 | 99·72 | 98·75 | 97·86 | 98·08 | 98·82 | 98·36 | 100·00 |

* The loss consists partly of osmium.

† Quartz.

The following table contains the results of analyses of platinum-ore from various localities by Deville and Debray.

| | Columbia. | | | California. | | | Oregon. | Spain. | Australia. | | Russia. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Platinum . . . | 86·20 | 80·00 | 76·82 | 85·50 | 79·85 | 76·50 | 51·45 | 45·70 | 59·8 | 61·40 | 77·50 | 78·4 |
| Iridium . . . | 0·85 | 1·55 | 1·18 | 1·05 | 4·20 | 0·85 | 0·40 | 0·95 | 2·2 | 1·10 | 1·45 | 4·3 |
| Rhodium . . . | 1·40 | 2·50 | 1·22 | 1·00 | 0·65 | 1·95 | 0·65 | 2·65 | 1·5 | 1·85 | 2·80 | 0·3 |
| Palladium . . | 0·50 | 1·00 | 1·14 | 0·60 | 1·95 | 1·30 | 0·15 | 0·85 | 1·5 | 1·80 | 0·85 | 1·4 |
| Gold . . . | 1·00 | 1·50 | 1·22 | 0·80 | 0·55 | 1·20 | 0·85 | 3·15 | 2·4 | 1·20 | * | 0·4 |
| Copper . . . | 0·60 | 0·65 | 0·88 | 1·40 | 0·75 | 1·25 | 2·15 | 1·05 | 1·1 | 1·10 | 2·15 | 4·1 |
| Iron . . . | 7·80 | 7·20 | 7·43 | 6·75 | 4·45 | 6·10 | 4·30 | 6·80 | 4·3 | 4·55 | 9·60 | 11·7 |
| Osm-iridium . . | 0·95 | 1·40 | 7·98 | 1·10 | 4·95 | 7·55 | 37·30 | 2·85 | 25·0 | 26·00 | 2·35 | 0·5 |
| Sand . . . | 0·95 | 4·35 | 2·41 | 2·95 | 2·60 | 1·50 | 3·00 | 35·95 | 1·2 | 1·20 | 1·00 | 1·4 |
| Lead . . . | . . | . . | . . | . . | . . | 0·55 | | | | | | |
| Osmium and loss . | . . | . . | . . | . . | 0·05 | 1·25 | . . | 0·05 | 0·8 | . . | 2·30 | |
| | 100·25 | 100·15 | 100·28 | 101·15 | 100·00 | 100·00 | 100·25 | 100·00 | 99·8 | 100·20 | 100·00 | 100·5 |

**Methods of Analysis.** The first complete method of analysing platinum-ore was given by Berzelius in 1828; this will be found fully described in *Gmelin's Handbook* (vi. 259–264). Claus in 1854 (*Beiträge zur Geschichte der Platinmetalle*) proposed a simpler and in some respects more exact method, and recently another method has been devised by Deville and Debray (Ann. Ch. Phys. [3] lvi. 385; Jahresb. 1859, p. 243).

*Claus's Method.* *a. Mechanical preparation of the ore and solution in nitromuriatic acid.*—This part of the operation is performed by Claus in the same manner as by Berzelius.

The ore, after being freed from grains of foreign matter by mechanical separation, and by the magnet, is treated with dilute hydrochloric acid, which dissolves ferric oxide and metallic iron. It is then heated in a tubulated retort having a cooled receiver adapted to it, with concentrated hydrochloric acid, to which strong nitric acid is added from time to time, as the action diminishes in intensity. An excess of nitric acid must be avoided, because it would decompose the chloride of iridium, and cause the separation of oxide of iridium on evaporation. The heat is continued till the residue in the retort becomes syrupy and solidifies on cooling; the saline mass is dissolved in a small quantity of hot water; and the solution is carefully decanted from the insoluble residue. The distillate, which has a yellowish colour arising from chloride of platinum which has spirted over, is then poured upon the residue, and distilled again, without boiling, whereupon a colourless distillate of dilute osmic acid is obtained. Should the residue still contain any soluble matter, it must be again treated in the same manner with aqua-regia.

The distillate is neutralised with ammonia or lime; saturated with sulphydric acid gas in a bottle nearly filled with it; and set aside for some days with the bottle closed till the precipitate settles down; after which the watery liquid is separated from the sulphide of osmium by decantation and filtering. In this manner the quantity of osmium in the distillate is determined (p. 244).

*β. Separation of the other metals.*—The mode of separation is founded: first, on the insolubility of chloroplatinate of ammonium, and the corresponding salts of iridium, osmium and ruthenium, also of chlororuthenite of ammonium, in sal-ammoniac solution; secondly, on the solubility of chloriridite of ammonium (iii. 318), and of the corresponding rhodium-salt in sal-ammoniac solution; and thirdly, on the convertibility of chloriridate of ammonium into chloriridite by the action of sulphydric acid.

The solution containing the platinum &c., after being separated from the residue, is evaporated to dryness over the water-bath in a porcelain basin, and heated for some time in a sand-bath to 140°—150° in order to convert the tetrachloride of iridium into trichloride. A small quantity of hydrochloric acid is then added; the whole is dissolved in water, and mixed with a strong solution of sal-ammoniac; and the resulting precipitate of chloroplatinate of ammonium is collected on a weighed filter, washed with dilute sal-ammoniac, then with alcohol of 0·80°: when dried and weighed it gives the quantity of platinum. This platinum contains merely a small quantity of iridium, from which it may be freed by solution in nitromuriatic acid containing an excess of nitric acid. The iridium is then left behind, and may be calcined with the filter, then reduced by hydrogen and weighed.

The mother-liquors from which the chloroplatinate of ammonium has separated, are mixed with the wash-waters, and exposed to the action of a current of chlorine till they assume the brown-red colour of tetrachloride of iridium, then evaporated to dryness over the water-bath; and the dry mass reduced to fine powder is treated with alcohol of 80 per cent. till the washings become quite colourless. The filtered liquid contains all the iron and copper—which may be determined by the ordinary methods—with scarcely any traces of the platinum-metals.

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* Gold (if any) counted with the loss.

The residue insoluble in alcohol contains all the platinum-metals except osmium; the quantity of ruthenium in it is however too small to be estimated. By washing it with a dilute solution of sal-ammoniac, till the liquid, which is red at first, runs off colourless, the rhodium and palladium are entirely dissolved, while platinum and iridium remain behind (*A*). The solution is evaporated to dryness; the dry residue is calcined in a closed platinum crucible, then reduced by hydrogen, and the mixture of rhodium and palladium is weighed. The two metals are then treated with nitromuriatic acid; the resulting solution, which contains all the palladium together with a little rhodium, is evaporated nearly to dryness, mixed with a drop of caustic soda-solution, and precipitated with cyanide of mercury; and the precipitate, after washing, drying, and ignition, is reduced with hydrogen and weighed as palladium. The quantity of this metal deducted from the total weight of the two metals, gives the weight of the rhodium.

The residue (*A*) containing platinum and iridium is heated with water to the boiling point, and mixed with a quantity of aqueous sulphydric acid, sufficient to convert the tetrachloride of iridium into trichloride. The liquid, highly concentrated but not filtered, is next mixed with a strong solution of sal-ammoniac, whereby all the platinum is precipitated, and the iridium retained in solution. The liquid is filtered; the precipitate washed with a strong solution of sal-ammoniac; the filtrate evaporated to dryness; the salt carefully ignited; and the iridium weighed after reduction in a stream of hydrogen. The platinum-salt is likewise ignited, and the quantity of platinum which remains is added to that previously obtained. To prevent loss, it is advisable to wrap up the saline mixture, which contains a large quantity of sal-ammoniac, in filter-paper, and ignite it as carefully as possible.

The residue insoluble in nitromuriatic acid is disintegrated, according to Wöhler's method (iii. 314), by mixing it with chloride of sodium, and igniting it three times in a stream of moist chlorine. The mass is then digested several times with water, and the united solutions, which, besides a large quantity of common salt, contain all the platinum-metals (but only a small quantity of palladium) and considerable quantities of iron and copper, are strongly concentrated and treated with chlorine to convert the trichloride of iridium into tetrachloride. A strong solution of sal-ammoniac is then added, which after a while throws down the whole of the platinum, iridium, ruthenium, and osmium, while rhodium, palladium, iron and copper remain in solution. The precipitate is washed with water containing sal-ammoniac, then dissolved in boiling water, and the solution is kept for some time at the boiling heat, and mixed with a few drops of ammonia, which precipitates osmium and ruthenium. To separate these metals, the precipitate is fused in a silver crucible with a mixture of 2 pts. nitrate and 1 pt. hydrate of potassium, and the fused mass is treated with distilled water, whereby a solution of osmiate and rutheniate of potassium is obtained. The ruthenium is then precipitated as trioxide by nitric acid, and separated from any osmium that it may still contain by distillation with nitric acid; the osmium in the solution is likewise separated in the same manner. The residue containing ruthenium and nitrate of potassium is treated with hydrochloric acid, and the liquid is concentrated by evaporation. On cooling it deposits crystals of nitre, and the mother-liquor, on further concentration, deposits chlororutheniate of potassium, from which the ruthenium may be separated in the metallic state (see Ruthenium).

The solution containing the platinum and iridium is treated for the separation of these metals in the manner above described. See also Osmiridium (p. 240).

*Deville and Debray's method.*—1. To determine the sand (quartz, zircon, chrome-iron, and titaniferous iron), 2 grammes of the ore are fused in a small earthen crucible, with 7 to 10 grammes of pure granulated silver and 10 grammes of fused borax; and after cooling, the button of silver which contains the osmium, platinum, and all the other metals, is detached, and digested if necessary, with weak hydrofluoric acid, to remove the last portions of borax,—then dried, heated to redness, and weighed. The weight of the button deducted from the sum of the weights of the ore and the silver employed, gives the quantity of sand in the ore.

2. To determine the Osmiridium.—Two grammes of the ore are digested at 70° with nitromuriatic acid (composed of 2 vols. strong hydrochloric and 1 vol. strong nitric acid) till the platinum &c. is completely dissolved, renewing the nitromuriatic acid till it no longer becomes coloured after 12 or 15 hours' action. The solution is very carefully decanted from the residue (any spangles of osmiridium that it may deposit on standing being collected on a filter and added to the residue); and this residue is thoroughly washed by decantation, then dried and weighed. The

difference between this weight and that of the sand previously determined gives the weight of the osmiridium.

The reguline mass free from sand, obtained in the first stage of the process, may also be used for the estimation of the osmiridium, the silver contained in it being dissolved out by nitric acid, and the residue, which contains the osmiridium, treated in the manner just described.

3. To determine the platinum and iridium, the solution obtained by treating the ore with nitromuriatic acid is evaporated nearly to dryness at a gentle heat; the residue is treated with a small quantity of water (in which it should dissolve completely), then with a volume of pure alcohol equal to twice that of the water; a large excess of pure crystallised chloride of ammonium is added; and the liquid is gently warmed till the sal-ammoniac is nearly dissolved, then stirred, and left at rest for 24 hours. The resulting precipitate containing the platinum and iridium (but not the whole) is collected on a filter, washed with alcohol of 75 per cent., then dried and ignited at the lowest possible temperature—strips of paper moistened with oil of turpentine being repeatedly thrown into the crucible after the filter has been burned, in order to reduce the oxide of iridium and expel the last traces of osmium,—and finally heated to whiteness till the weight becomes constant. The mixture of platinum and iridium thus obtained is weighed and digested at 40°—50°, with nitromuriatic acid diluted with four or five times its weight of water, the liquid being renewed from time to time till it no longer becomes coloured; the undissolved portion is pure iridium. The liquid decanted from the above-mentioned precipitate (containing platinum and iridium) formed by the sal-ammoniac, is evaporated till a great part of the sal-ammoniac has crystallised out, and filtered when cold; it then deposits a small additional quantity of platiniferous chloriridiate of ammonium, which is to be washed with solution of sal-ammoniac, then with alcohol, and treated as above.

4. The alcoholic liquid freed from platinum and iridium by precipitation with sal-ammoniac still contains palladium, iron, copper, gold and rhodium. It is freed from alcohol by warming, from sal-ammoniac by digestion with excess of nitric acid (which resolves this salt into nitrogen and hydrochloric acid), then evaporated nearly to dryness. The residue is completely dried in a porcelain crucible which can be covered, then moistened with concentrated aqueous sulphide of ammonium, carefully and completely dried after addition of 2 or 3 pts. of pure flowers of sulphur, and finally heated to bright redness, the porcelain crucible being placed within a covered earthen crucible, so that lumps of charcoal may be placed between the two, and ignited from above downwards. The weighed contents of the crucible, consisting of reduced palladium, sulphide of iron, $Fe^3S^4$, sulphide of copper, $Cu^2S$, and metallic gold and rhodium, are digested for some time at 70° with rather strong nitric acid, which dissolves palladium, iron and copper; the solution is evaporated to dryness; the residue heated to dull redness; and the ignited mass treated with somewhat dilute hydrochloric acid which dissolves the iron and copper as ferric and cupric chlorides, leaving palladium undissolved. On evaporating the solution to dryness at 100°, and treating the residue with aqueous ammonia, the copper dissolves as cupric chloride, while the iron remains as ferric oxide. The ammoniacal solution is concentrated, the copper converted into nitrate by addition of nitric acid and evaporation, then into cupric oxide by igniting the residue, and weighed in that form. Lastly, the portion of the contents of the porcelain crucible, insoluble in nitric acid, consisting of gold and rhodium, is digested in weak nitromuriatic acid, which dissolves the gold and leaves the rhodium.

It is by this method that the analyses of platinum-ore, the results of which are given at page 680, were made. For the commercial assay of platinum-ores, Déville and Debray give the following method.

The gold is extracted by repeatedly treating the ore with small quantities of mercury and weighed after distilling off the mercury from the liquid amalgam. This process makes the amount of gold rather too small; on the other hand, it is obtained slightly in excess by treating the ore with weak nitromuriatic acid, evaporating, and igniting the residue.

The sand is determined as above described (p. 681).

To determine the platinum, 50 grms. of the ore are fused with 75 grms. of pure lead, 50 grms. of pure well crystallised galena, and 10 to 15 grms. of borax, the heat being raised to the melting point of silver and kept at that temperature till no more grains of platinum can be perceived on stirring the fused mass with a pipe-stem, after which the heat is increased and 50 grms. of litharge are gradually added in proportion as it is reduced. The whole is then left to cool, and the reguline mass, after being cleansed from slag, is weighed. The mass, weighing about 200 grms., contains the platinum-metals alloyed with lead, also the osmide of iridium mixed up with its lower part, while the iron and copper have passed into the slag. The lower portion of this regulus

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is next sawn off; the upper (amounting to about $\frac{9}{10}$ths of the whole) is weighed together with the shavings; a portion of it, amounting to $\frac{1}{9}$th, is cupelled with an exactly weighed portion of silver (equal to 5 or 6 times the weight of platinum supposed to be present), and if necessary with an additional quantity of lead, at the temperature required for a gold assay. The platinum then remains alloyed with silver, and the weight of the latter, diminished by that of the silver added, gives the weight of the platinum, and ten times this weight is the total amount of platinum in the portion of ore taken for the assay. This result is however affected with a slight error, arising from the small quantity of osmiridium in the lower part of the regulus. To avoid this source of inaccuracy, the following method may be adopted.

The lower part ($\frac{1}{10}$th) of the regulus is heated with ten times its weight of nitric acid diluted with an equal volume of water, till all the lead is dissolved, and nothing is left but a fine powder consisting of platinum and osmiridium. This residue, after being carefully washed by decantation, first with acidulated, then with pure warm water, is dried and weighed, then treated with nitromuriatic acid, which dissolves out the platinum; and the osmiridium which remains undissolved is finally washed, dried, and weighed. Its weight, deducted from that of the residue insoluble in nitric acid, gives the weight of the platinum.

The proportion of platinum found by the assay must however be diminished by about 4 per cent. to allow for the palladium, rhodium, and iridium which exist in the ore always to the amount of 4 to 5 per cent., and are not separated by the process just described.

Platinum-residues.—For the analysis of the matters which remain undissolved when platinum-ore is digested in nitromuriatic acid (insoluble residues), and for those obtained by precipitation with metallic iron from the solution previously freed from platinum and palladium (precipitated residues), Deville and Debray give the following methods.

*α.* The *insoluble residues* contain all the platinum-metals, but consist chiefly of osmiridium and sand in very variable proportions. 50 grms. of the residue are introduced into a crucible together with 150 to 200 grms. litharge and 50 to 100 grms. lead—the lead at the bottom, then the mixture of platinum-residue and litharge, and pure litharge at the top—and heated to redness for half-an-hour, stirring from time to time with an earthenware rod; after which the crucible is left to cool and the reguline mass is freed from slag (the litharge may be completely removed by a few hours' treatment with hot acetic acid and subsequent brushing). This mass is treated with dilute nitric acid at 100° till the lead is completely dissolved; the solution, which contains lead and palladium, is freed from lead by a slight excess of sulphuric acid, then evaporated nearly to dryness at a temperature not exceeding 120°; the residue is treated with water; and from the resulting solution, the palladium is precipitated as cyanide. The residue left undissolved by the nitric acid is thoroughly washed with boiling water slightly acidulated with nitric acid; then dried and weighed (let the weight be called $A$); treated with nitromuriatic acid, which quickly dissolves the platinum together with a little iridium and rhodium; and the weight ($B$) of the undissolved matter is determined: this is osmiridium. The nitromuriatic acid solution contains chiefly platinum, the quantity of which is nearly equal to $A - B$. Its weight may be more exactly determined, together with that of the iridium, by precipitating a finely divided mixture of the two metals in the manner given at page 681, and dissolving out the platinum with weak nitromuriatic acid. The rhodium may also be determined by the method already given for the analysis of platinum-ores.

*β.* The *precipitated residues* are analysed nearly in the same manner, a smaller quantity, however, viz. 10 grms., being taken, and fused with 10 to 15 grms. lead and 30 to 40 grms. litharge. The resulting metallic mass contains—besides lead, which must be carefully precipitated as sulphate—palladium, to be precipitated as cyanide in the manner above described, and rhodium, which may be determined by evaporating the filtered liquid to dryness, and reducing the residue with addition of sulphur in the manner described at page 682, No. 4. From the residue insoluble in nitric acid, the platinum is dissolved by nitromuriatic acid, together with small quantities of iridium and rhodium, to be determined by methods already detailed, and there then remains a residue consisting chiefly of iridium together with a small quantity of osmiridium (which was probably suspended in the liquids from which the precipitated residues were obtained). The slag, consisting chiefly of litharge, contains the iron and copper which were present in the precipitated residues.

The following are the results of the analysis of several platinum residues made by this method.

*Insoluble Residues.*

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Osmiridium . . . | 12·35 | 34·00 | 29·15 | 92·50 | 96·10 | 94·20 | 26·60 | 83·60 | 60·10 |
| Palladium . . . | 0·18 | . . | . . | 0·02 | 0·02 | 0·02 | 0·70 | . . | 0·37 |
| Platinum with traces of Iridium . . | 0·53 | . . | 0·90 | 0·78 | 0·18 | 0·86 | 7·00 | . . | 2·14 |
| Rhodium . . . | 0·15 | . . | 0·13 | 0·10 | 0·20 | 0·88 | 0·20 | . . | 1·36 |
| Sand . . . . | 86·79 | 66·00 | 69·82 | 6·60 | 3·50 | 4·04 | 65·50 | 16·40 | 36·03[*] |
| | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

*Precipitated Residues.*

| | *a.* |
|---|---|
| Palladium . . . . . . | 0·8 |
| Platinum . . . . . . | 0·8 |
| Rhodium . . . . . . | 2·1 |
| Rhodium, Iridium and Osmiridium | 21·8 |
| Common metals . . . . | 74·2 |
| | 100·0 |

| | *b.* |
|---|---|
| Osmiridium . . . . | 2·2 |
| Palladium . . . . . | 1·2 |
| Platinum . . . . . | 0·5 |
| Iridium . . . . . | 23·3 |
| Rhodium . . . . . | 6·4 |
| Common metals . . . | 66·4 |
| | 100·0 |

*a.* From the Russian mint: small irregular masses.
*b.* Black powder with crystalline scales.

*Analysis of Osmiridium* according to Deville and Debray.—The sand is first determined by the method already given (p. 681). The osmiridium is then disintegrated by fusion with metallic zinc as described under Iridium (iii. 315), then mixed with 5 pts. of barium-peroxide, or 3 pts. peroxide and 1 pt. nitrate of barium, and heated moderately for an hour or two in a silver crucible having a close-fitting cover. The mass when cold is detached by pressing the sides of the crucible, and transferred to a capacious porcelain dish, in which it is mixed with hydrochloric acid and a little nitric acid (care being taken to avoid loss by spirting). The mixture is heated to boiling till the odour of osmic acid has entirely disappeared, then evaporated to dryness slowly and at a moderate heat; the residue is digested with warm water and a little acid; and the solution is decanted from a small portion of silica and osmiridium, the weight of the latter being determined and allowed for. From the solution the barium is precipitated by a quantity of titrated sulphuric acid, equivalent to the weight of the peroxide and nitrate of barium used (a very slight excess, however, does no harm); the filtrate is treated with sal-ammoniac to precipitate the iridium, ruthenium and platinum; this precipitate is reduced; the platinum is dissolved out of it by dilute nitromuriatic acid; and the residue is fused with nitrate and hydrate of potassium, whereby it is resolved into iridium which remains almost unattacked, and ruthenium which dissolves. The rhodium (together with any iron and copper that may be present) remains in the liquid from which the iridium &c. has been precipitated by sal-ammoniac, and is reduced therefrom by the method already described (p. 682). The osmium is estimated by loss, a method which Deville and Debray regarded as more trustworthy than the collection of the osmic acid and the determination of the osmium therefrom.

The composition of several samples of the mineral as determined by Deville and Debray, and others, is given under Iridosmine (iii. 324).

**PLATINUM-RESIDUES.** See page 683.

**PLATINUM-SPONGE.** Finely divided platinum, obtained by igniting chloroplatinate of ammonium (p. 663).

**PLATOSAMINE.** $NH^2Pt$.—The ammonia-base supposed by Gerhardt to exist in the ammonio-platinous compounds. See Platinum-bases, Ammoniacal (p. 678).

**PLATOSETHYLAMINE, PLATOSOPYRIDINE.** Hypothetical bases analogous to platosamine. (See Platinum-bases, Organic, p. 679.)

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[*] With the common metals and especially silver.

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**PLATTNERITE.** Native peroxide of lead, $\text{PbO}^2$, from Leadhills, Scotland.

**PLEONAST.** Ferruginous spinel (see SPINEL).

**PLEUROCLASE.** Syn. with WAGNERITE (see PHOSPHATES, p. 569).

**PLINIAN.** See MISPICKEL (iii. 1026).

**PLOCARIA LICHENOÏDES.** One of the algæ from which gelose is obtained (ii. 829).

**PLOMBGOMME.** Syn. with PLUMBO-RESINITE.

**PLOMBIERIN.** Syn. with BAREGIN (i. 509).

**PLOMBIERITE.** A hydrated silicate of calcium, $\text{Ca}''\text{SiO}^3.2\text{H}^2\text{O}$, formed by the action of a hot mineral spring at Plombières on an old Roman mortar. It is deposited as a gelatinous nodular mass, which on exposure to the air becomes hard, opaque and snow-white. (Danbrée, Ann. Min. [5] xiii. 214.)

**PLUM.** See PRUNUS.

**PLUMBAGIN.** The acrid principle of the root *Plumbago europæa.* It is obtained by repeatedly boiling the ethereal extract of the root with water, whence it is deposited on cooling, and may be purified by crystallisation from alcohol or ether-alcohol. It crystallises in delicate needles or prisms often grouped in tufts; has a styptic saccharine taste, with acrid biting after-taste; melts very easily, and partly volatilises unaltered when heated. It is neutral, nearly insoluble in cold, more soluble in boiling water, very soluble in alcohol and ether. It dissolves with yellow colour in strong sulphuric and in fuming nitric acid, and is precipitated by water in yellow flocks. Alkalis change the colour of the solution to a fine cherry-red; acids restore the yellow colour. Basic acetate of lead also colours it red, and forms a crimson precipitate. (Dulong, J. Pharm. xiv. 441.)

**PLUMBAGO.** See CARBON (i. 758).

**PLUMBETHYLS.** See LEAD-RADICLES, ORGANIC (iii. 561).

**PLUMBIC OCHRE.** Native protoxide of lead (see LEAD, iii. 549).

**PLUMBOCALCITE.** An isomorphous mixture of the carbonates of lead and calcium, $\text{Pb}''\text{CO}^3.32\text{Ca}''\text{CO}^3$, occurring in rhombohedral forms at Leadhills, and in the High Pirn Mine, Wanlockhead, Lanarkshire.

**PLUMBORESINITE.** *Plombgomme, Bleigummi, Gummispath.*—A lead-mineral resembling gum arabic in colour and appearance, found at Huelgoet in Brittany, at Nussière near Beaujen, at Roughten Gill, Cumberland, and at Mine La Motte, Missouri. According to Berzelius, it is a hydrated aluminate of lead, $\text{Pb}''\text{O}.\text{Al}^2\text{O}^3.6\text{H}^2\text{O}$ or $\text{Pb}''\text{Al}^2\text{O}^4.6\text{H}^2\text{O}$. Damour and Dufrénoy, on the other hand, found in it about 8 per cent. phosphoric anhydride, and according to their analysis it would appear to be a mixture or compound of phosphate of lead with hydrate of alumina, $\acute{\text{Pb}}{}^3\text{P}^2\text{O}^8.6\overline{\text{Al}}{}^2\text{H}^2\text{O}^4$. (Dana, ii. 431.)

**PLUMBOSTIB.** Syn. with BOULANGERITE (i. 651).

**PLUMOSITE.** Syn. with HETEROMORPHITE (iii. 151).

**PNEUMATIC TROUGH.** See GASES, COLLECTION AND PRESERVATION OF (ii. 806).

**PNEUMIC ACID.** An acid existing, according to Verdeil (Compt. rend. xxxiii. 604), in the parenchyma of the lungs of most animals. It is very soluble in water, insoluble in cold alcohol, but soluble in boiling alcohol, whence it crystallises in stellate groups of shining needles, which do not give off any water at 100°. It contains carbon, hydrogen, nitrogen, oxygen, and sulphur, forms crystallisable salts, and decomposes carbonates (Gerh. iii. 924).

**POLARISATION, ELECTRICAL.** See ELECTRICITY (ii. 399, 429).

**POLARISATION, MAGNETIC.** See MAGNETISM (iii. 757, 763).

**POLARISATION OF LIGHT.** See LIGHT (iii. 652).

**POLEY-OIL.** A volatile oil obtained from the herb of *Mentha Pulegium* at flowering time, by distillation with water, and having, according to Kane, the composition of camphor, $\text{C}^{10}\text{H}^{14}\text{O}$. It is yellowish, has an aromatic odour, a specific gravity of 0·9271 to 0·939; boils between 182° and 185°, and leaves a small quantity of solid matter when rectified. (Handw. d. Chem. vi. 615.)

**POLIANITE.** A variety of native peroxide of manganese occuring at Platten in

Bohemia, and, together with pyrolusite, at Schneeberg and Johannisberg in Saxony. It crystallises, like pyrolusite, in trimetric forms, but differs from it in the proportions of its axes, and in cleaving distinctly parallel to the brachydiagonal only, whereas pyrolusite cleaves parallel to all three axes. It is also distinguished by greater hardness.

| | a. | | b. | | c. | ∞P : ∞P. | Hardness. |
|---|---|---|---|---|---|---|---|
| Pyrolusite | 1 | : | 1·066 | : | 0·776 | 93° 40′ | 2·25 |
| Polianite | 1 | : | 1·0513 | : | 0·6317 | 92° 52′ | 6·5 to 7 |

(Dana, ii. 131; Handw. vi. 615.)

**POLIENE.** Völckel's name for one of the compounds obtained by heating sulphocyanate of ammonium (*q. v.*) above 300°. Völckel regards it as isomeric with melamine or cyanuramide (ii. 287); but, according to Liebig, it is identical with melam (iii. 865) (see *Gmelin's Handbook*, ix. 484).

**POLISHING POWDER.** Very finely divided ferric oxide, used for polishing optical glasses, Daguerréotype plates, &c.

**POLISHING SLATE.** *Polirschiefer.*—A porous, slaty, fine-earthy rock, mostly of yellowish-white colour, consisting almost entirely of the siliceous shells of infusoria (Ehrenberg). That occurring on the Kritschelberg near Bilin, in Bohemia, was found by Baumann (*Rammelsberg's Mineralchemie*, p. 136) to contain 87·58 per cent. silica, 2·04 alumina and ferric oxide, 1·09 lime, 0·30 magnesia, and 8·89 water. In some places it is found to be converted into a semi-opaline substance.

**POLLUX.** A silicate of aluminium and cæsium, occurring, together with Castor (p. 381), in the island of Elba. It resembles analcime in form; is colourless and transparent; has a conchoïdal fracture with vitreous lustre on the fractured surface. Hardness = 6·5. Specific gravity = 2·900. When heated it gives off a little water, and becomes transparent, and when heated on platinum-wire with a little fluoride of ammonium, and then moistened with hydrochloric acid, it exhibits in the spectroscope the two blue lines of cæsium, together with the sodium-lines. Gives by analysis 44·03 per cent. silica, 15·97 alumina, 0·68 ferric oxide, 0·68 lime, 34·07 oxide of cæsium, 3·88 oxide of sodium, and 2·40 water = 101·71. (F. Pisani, Bull. Soc. Chim. [2] i. 456.)

Pollux was discovered by Breithaupt, and imperfectly analysed by Plattner (with a loss of 7 per cent.), who regarded it as a silicate of aluminium, potassium, and sodium.

**POLYADELPHITE.** A brownish-yellow garnet from the Franklin furnace, New Jersey, containing, according to Weber (*Rammelsberg's Mineralchemie*, p. 693), 34·83 per cent. silica, 1·12 alumina, 28·73 ferric oxide, 8·82 manganous oxide, 24·05 lime, and 1·42 magnesia (= 98·97).

**POLYARGITE.** A rose-coloured granular variety of anorthite from Tunaberg in Sweden, containing, according to A. Erdmann (*Rammelsberg's Mineralchemie*, p. 593):

| $SiO^2$. | $Al^2O^3$. | $Fe^2O^3$. | $Mn^2O^3$. | $Ca''O$. | $Mg''O$. | $Na^2O$. | $K^2O$. | $H^2O$. | |
|---|---|---|---|---|---|---|---|---|---|
| 45·12 | 35·64 | 0·14 | 0·30 | 5·88 | 0·26 | 0·67 | 6·93 | 4·92 | = 99·86. |

**POLYBASITE.** A sulpharseno-antimonite of silver and copper, occurring in short tabular hexagonal prisms, oP . ∞P . P, having the principal axis = 1·4132. Angle P : P in the terminal edges = 129° 32′; in the basal edges = 117°; oP : P = 121° 30′. The terminal planes are triangularly striated parallel to the terminal edges. Cleavage basal, imperfect. It occurs also massive and disseminated. Hardness = 2—3. Specific gravity = 6·214. Lustre metallic. Colour iron-black; thin tabular crystals, however, appear cherry-red by transmitted light. Streak iron-black. Opaque. Fracture uneven.

*Analyses: a.* from Schemnitz; *b.* from Freiberg (H. Rose, Pogg. Ann. xv. 573); *c.* from Cornwall (Jay's *Miscellaneous Chemical Researches*, Gottingen, 1853, p. 21); *d.* Durango, Mexico (H. Rose).

| | S. | Sb. | As. | Ag. | Cu. | Fe. | Zn. | | |
|---|---|---|---|---|---|---|---|---|---|
| *a.* | 16·83 | 0·25 | 6·23 | 72·43 | 3·04 | 0·33 | 0·59 | = | 99·70 |
| *b.* | 16·35 | 8·39 | 1·17 | 69·99 | 4·11 | 0·29 | . . | = | 100·30 |
| *c.* | 15·87 | 5·46 | 3·41 | 72·01 | 3·36 | 0·34 | . . | = | 100·45 |
| *d.* | 17·04 | 5·09 | 3·74 | 64·29 | 9·93 | 0·06 | . . | = | 100·15 |

The mineral is an isomorphous mixture of sulphur-salts $(Ag; Cu)^9(Sb; As)S^6$ or $(Ag^2S; Cu^2S)^9(Sb^2S^3; As^2S^3)$, in which

| | | Ag | : | Cu |
|---|---|---|---|---|
| in *a* and *b* | = | 9 | : | 1 |
| in *c* | = | 10 | : | 1 |
| in *d* | = | 4 | : | 1 |

| | | Sb | : | As |
|---|---|---|---|---|
| in *a* | = | 1 | : | 40 |
| in *b* | = | 9 | : | 2 |
| in *c* and *d* | = | 1 | : | 1 |

Stephanite and iron pyrites occur as pseudomorphs after polybasite. (Dana, ii. 85.)

**POLYCHREST-SALT.** An old name for neutral sulphate of potassium; also for sodio-potassic tartrate.

**POLYCHROÏLITE.** A silicate found in gneiss at Krageröe, Norway, crystallised in six-sided prisms of about 120° with flat summits; also massive and reniform. Hardness = 3—3·5. Lustre greasy. Colour blue, green, brown, and red, rarely white. According to an analysis by Dahl (*Leonh. Jahrb.* 1846, p. 288), it contains 52 per cent. silica, 37 alumina, 7 magnesia, 3 ferric oxide, together with lime and water. Scheerer found less alumina and 6 per cent. water.

**POLYCHROITE.** Syn. with Safranin.

**POLYCHROME.** Syn. with Aesculin (i. 60).

**POLYCHROMIC** or **POLYCHROMATIC ACID.** Syn. with Aloetic Acid (i. 148).

**POLYCRASE.** See Niobium (p. 57).

**POLYETHYLENIC ALCOHOLS.** See Ethylene, Hydrates of (ii. 576).

**POLYGALIC ACID** or **POLYGALIN.** Syn. with Senegin.

**POLYGAMARIN.** The name applied by Reinsch (Buchn. Repert. xvii. 289) to a crystalline bitter substance which remains, together with wax and chlorophyll, when the alcoholic extract of *Polygala amara* is treated with ether.

**POLYGONUM FAGOPYRUM.** Buckwheat (i. 685).

**POLYGLYCERIC ALCOHOLS.** See Glyceryl, Hydrates of (ii. 894).

**POLYHALITE.** A crystalline mixture or compound of various sulphates represented by the formula $M^2SO^4.2H^2O$, occurring with rock-salt in various localities (Ischl, Aussee, Hallstadt, Berchtesgraden, Graünd, Stassfurth, Vic in the dept. of the Meurthe, &c.), in rhombic prisms of 115°. The composition varies considerably, as shown by the following analyses: *a.* from Ischl (Stromeyer, *Untersuchungen*, i. 144);—*b.* from Hallstadt (v. Hauer, Wien. Akad. Ber. xi. 385);—*c.* from Ebensee (v. Hauer);—*d.* from the rock-salt of Stassfurth (Reichardt, Jahresb. 1862, p. 757).

| | $Ca''SO^4$. | $Mg''SO^4$. | $K^2SO^4$. | NaCl. | $Fe^2O^3$. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|
| *a.* | 44·47 | 20·03 | 27·70 | 0·19 | 0·34 | 5·95 | = | 98·95 |
| *b.* | 56·41 | 11·04 | 14·81 | 12·16 | . . | 5·58 | = | 100 |
| *c.* | 61·18 | 13·53 | 19·12 | 0·28 | 0·41 | 6·05 | = | 100·52 |
| *d.* | 43·44 | 20·56 | 26·22 | 0·58 | $Mg''Cl^2$ | 7·47 | = | 98·27 |

**POLYLACTYL-COMPOUNDS.** See Lactic Acid and Lactic Ethers (iii. 461—464).

**POLYLITE.** A variety of augite from Hoboken, New Jersey, containing, according to Thomson (*Outlines*, i. 495), 40·04 silica, 9·42 alumina, 34·08 ferrous oxide, 6·6 manganous oxide, 11·54 lime, and 0·40 water.

**POLYMERISM.** Bodies are said to be polymeric when they have the same percentage composition, but different molecular weights; the olefines $C^nH^{2n}$ for example (see Isomerism, iii. 415).

**POLYMIGNITE.** A mineral occurring at Fredriksvärn, Norway, in trimetric crystals sometimes an inch long, imbedded in felspar and zircon-syenite. Axes $a : b : c = 1 : 1·0308 : 0·7252$. Angle $\infty P : \infty P = 91·44'$; $oP : \breve{P}\infty = 144° 3'$. Observed combination $\infty\breve{P}\infty . oP . 2\bar{P}2 . 4\breve{P}\infty . 2\breve{P}\infty . \bar{P}\infty$. Cleavage parallel to $\infty\breve{P}\infty$ and $oP$ in traces. The crystals are usually slender and longitudinally striated. Hardness = 6·5. Specific gravity = 4·77—4·85. Lustre submetallic. Colour black. Streak dark brown. Opaque. Fracture conchoïdal. It contains, according to Berzelius (Kongl. Vetensk. Akad. Förhandl. 1824, ii. 339), 46·30 per cent. titanic oxide, 14·14 zirconia, 12·20 ferric oxide, 2·70 manganic oxide, 5·00 ceric oxide, 11·50 yttria, and 4·20 lime. The difficulty of separating the titanic oxide and zirconia renders the analysis somewhat uncertain.

**POLYMORPHISM.** A body is said to be polymorphous when it crystallises in two or more forms not derivable one from the other (see Dimorphism, ii. 331).

**POLYSILICIC ACIDS.** See Silicates.

**POLYSPHÆRITE.** Brown lead-ore from the Sonnenwirbel mine near Freiberg (p. 567).

**POLYTEREBENES.** Hydrocarbons polymeric with oil of turpentine (see Terebene).

**POLYTELITE.** See TETRAHEDRITE.

**POLYTHIONIC ACIDS.** See SULPHUR, OXYGEN-ACIDS OF.

**POLYXENE.** An old name of native platinum.

**POMPHOLYX.** An old name for impure zinc-oxide, sublimed in the roasting of zinc-ores and in the melting of brass: also called *Nihilum album*.

**PONGAMIA.** The seeds of *Pongamia glabra* contain 27 per cent. of a dark-yellow fat oil, having a specific gravity of 0·945, a poisonous odour and bitter taste, and solidifying at 8°. (Lepine, J. Pharm. [3] xl. 16.)

**POONAHLITE.** A variety of scolecite from Poonah in Hindostan.

**POPLAR-BUDS.** The buds of *Populus nigra* and P. *pyramidalis* contain a colouring matter called chrysinic acid, associated with salicin, a volatile oil, and a resinous substance. To extract the chrysinic acid, the alcoholic extract of the buds is treated with basic acetate of lead; the solution, freed from lead by sulphydric acid and filtered, is evaporated to dryness; and the residue is treated with water to remove salicin, then freed from resin by redissolving it in alcohol, and precipitating a second time with basic acetate of lead. The liquid, if left to itself, after being freed from lead, deposits, after a while, a white powder consisting of chrysinic acid, which may be purified by recrystallisation from alcohol.

Chrysinic acid, $C^{11}H^8O^3$, crystallises in thin fragile laminæ, perfectly white if preserved from contact with ammoniacal vapours. It is anhydrous, bears a heat of 200° without decomposing, and sublimes in fine needles at a higher temperature. It is nearly insoluble in water, soluble in boiling, less soluble in cold alcohol, soluble in ether.

Chrysinic acid dissolves with a fine yellow colour in strong sulphuric acid and in alkalis; baryta and lime also colour it yellow, but do not dissolve it easily. Nitric acid first colours it yellow, then decomposes it; acetic acid and hydrochloric acid have no action upon it. With iron-salts it forms a dirty-green precipitate; with neutral lead-acetate, no precipitate; with the basic acetate a slight precipitate, soluble in acetic acid. The alcoholic solution of the acid mixed with chloride of lime becomes yellow in the cold and red when heated.

*Chrysinate of potassium* crystallises in slender needles; the *ammonium-salt* is obtained by evaporation in spherical masses. The *barium-salt*, $C^{22}H^{14}Ba''O^6$, is obtained by adding a boiling alcoholic solution of chrysinic acid to an excess of baryta-water; and is deposited on cooling as a yellow powder. (J. Piccard, J. pr. Chem. xciii. 369; Bull. Soc. Chim. 1865, ii. 144.)

**POPPY.** The black poppy (*Papaver somniferum*, var. *nigrum*), which has red flowers and black seeds, is cultivated chiefly for the fat oil yielded by its seeds; the white poppy (*P. somniferum*, var. *album*, sometimes regarded as a distinct species and called *P. officinale*), having white flowers and seeds, for the production of opium.

The seeds of the white poppy (*Pavot blanc*, var. *à yeux ouverts*) have been found by Sacc (Ann. Ch. Phys. [3] xxvii. 473) to contain (exclusive of 3·03 per cent. hygroscopic moisture) 45·1 per cent. expressed oil, 9·5 fat oil extracted by ether, together with colouring and odoriferous matters, 3·5 volatile substance, 23·3 pectous substances, 12·6 protein-compounds, and 5·9 woody fibre.

The elementary composition of the seed, oil-cake, and oil, of the white poppy filtered without access of air, were found to be as follows:

| | Seed. | Oil-cake. | Oil-cake after exhaustion with ether. | Oil. |
|---|---|---|---|---|
| Carbon . . . . | 62·23 | 47·74 | 42·27 | 76·63 |
| Hydrogen . . . . | 9·20 | 6·76 | 6·04 | 11·63 |
| Nitrogen . . . . | 3·59 | 5·97 | 7·64 | |
| Oxygen and loss . . . | 17·97 | 28·94 | 30·85 | 11·74 |
| Ash . . . . . | 7·00 | 10·59 | 13·20 | |

The ash of the seed contained 0·82 $K^2O$, 4·47 $Na^2O$, 28·08 $Ca''O$, 4·33 $Mg''O$, 1·99 $SO^3$, 4·84 $SiO^2$, 17·66 $CO^2$, 37·81 $P^2O^5$.

Wildenstein (J. pr. Chem. liv. 200) has examined the ash of the seed and herb (*i. e.* stalks, leaves, and cleansed roots) of the black poppy, grown on the weathered Taunus slate near Wiesbaden. The dried seed yielded 6·12, the dried herb 7·86 per cent. ash, containing—

| | $K^2O$. | $CaO$. | $MgO$. | $Mn^2O^3$. | $SO^3$. | $SeO^2$. | $P^2O^5$. | $Fe^2PO^4$. | $KCl$. | $NaCl$. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Seed | 9·10 | 35·36 | 9·49 | trace | 1·92 | 3·24 | 30·98 | 0·81 | 7·15 | 1·94 | = 99·99 |
| Herb | 36·37 | 30·24 | 6·47 | trace | 5·09 | 11·40 | 1·28 | 4·14 | 2·50 | 2·51 | = 100·00 |

The air-dried seeds treated with nitric acid and chlorate of potassium gave 0·0828, and the air-dried herb, 0·0594 per cent. sulphur.

**POPPY-OIL.** *Huile d'œillette, Huile de Pavot.*—A fat drying oil obtained by expression from the seeds of the black poppy (*Papaver somniferum*, var. *nigrum*). It resembles olive-oil in aspect and odour, and is quite free from the narcotic properties of opium. Specific gravity = 0·9249 at −15°. It solidifies at −18°, and remains solid for a long time after the temperature has risen to −2°. It dissolves in 25 pts. of cold and 6 pts. of boiling alcohol, and mixes in all proportions with ether. Contains, according to Lefort, 77·20 per cent. carbon, 11·31 hydrogen, and 11·49 oxygen; see also Sacc's analysis of the oil from white poppy seeds (p. 688).

Poppy-oil yields substitution-products with chlorine and bromine. The *chlorinated oil* has a somewhat deeper yellow colour than the original oil, about the same consistence as castor oil and a specific gravity of 1·070 at 3°. It contains from 20·3 to 20·4 per cent. chlorine. The *brominated oil* containing 36·5 to 36·7 per cent. bromine, has a slight yellowish tinge, and the same consistence as the preceding: specific gravity = 1·279 at 2°.

Poppy-oil is used as an article of diet in the south of Germany and the north of France. It is employed in painting to mix with light colours, for which purpose it is first bleached by exposure to the sun in shallow vessels containing salt water. (For further details, see *Gmelin's Handbook*, xvi. 312.)

**POPULIN,** $C^{20}H^{22}O^8$, or *Benzoylsalicin*, $C^{13}H^{17}(C^7H^5O)O^7$.—This substance, discovered in 1831 by Braconnot (Ann. Ch. Phys. [2] xliv. 296), and investigated chiefly by Piria (Ann. Ch. Phys. [3] xxxiv. 278; xliv. 366), exists in the bark, leaves and root of the aspen (*Populus tremula*).

*Preparation.*—1. The aqueous decoction of the bark is precipitated with basic acetate of lead; the filtrate is freed from lead by sulphuric acid, then concentrated and boiled with animal charcoal; and the salicin, which likewise exists in the bark, is left to crystallise out. The mother-liquor yields with carbonate of potassium, a white precipitate of populin which must be recrystallised from boiling water (Braconnot). Herberger (Buchn. Repert. lv. 204), after precipitating with basic acetate of lead, removed the lead by passing carbonic acid into the liquid, and evaporated the filtrate to a syrup, from which the populin crystallised. From the decoction of the root-bark, populin crystallises after concentration (even without precipitation by basic acetate of lead) (Van de Ghejn).—2. The leaves of the aspen are boiled with water; the decoction is precipitated hot with basic acetate of lead; the populin carried down with the precipitate is dissolved out by boiling water; and the filtrate is evaporated to a syrup. The crystalline mass which separates is pressed between linen, heated to boiling with 60 pts. water and a little animal charcoal, and filtered at the boiling heat; the populin crystallises on cooling. (Braconnot.)

*Properties.*—Crystallised populin, $C^{20}H^{22}O^8.2H^2O$, forms white, silky, very light needles, which give off part of their water between 35° and 40°, and the rest (8·43 per cent. in all) at a temperature short of 100°. Anhydrous populin melts at 180° to a colourless liquid which solidifies to a vitreous mass on cooling. Populin has a sweet taste. It turns the plane of polarisation to the left, to an extent proportional to the quantity of salicin produced by its decomposition (*infra*). (Biot and Pasteur, Compt. rend. xxxiv. 607.)

Crystallised populin dissolves in about 2000 pts. of cold water (Braconnot), in 1896 pts. at 9° (Piria) and in 70 pts. boiling water (Braconnot). The cold solution deposits populin on being saturated with common salt; the solution saturated at the boiling heat deposits it on cooling. It dissolves at 14°—15°, in 100 pts. absolute *alcohol* (Biot and Pasteur); in boiling alcohol more abundantly than in boiling water, scarcely at all in *ether*.

Populin dissolves easily and without decomposition in cold *acids*, not too concentrated, and is precipitated partially by water, completely by alkalis (Braconnot, Koninck). According to Koninck, it dissolves also in aqueous *alkalis*, and is precipitated by acids.

Aqueous populin does not precipitate any *metallic salt* (Braconnot). It crystallises unaltered from solution in aqueous metallic salts, but may be made to combine with *oxide of lead*, forming a white substance nearly insoluble in water. (Koninck.)

Populin dissolves easily in cold concentrated *acetic acid*, and is precipitated therefrom partially by water, completely by *alkalis*. (Braconnot.)

*Decompositions.*—1. Fused populin heated to 180° gives off pungent vapours which condense in needles; at 220° it turns brown, but is obtained unaltered after solution in aqueous alcohol (Piria). When subjected to dry distillation, it swells up and yields empyreumatic oil, from which benzoic acid crystallises on cooling (Braconnot).—2. It *burns* with flame and an empyreumatic resinous odour (Braconnot).—3. Heated with sulphuric acid and *acid chromate of potassium*, it gives off large quantities of salicylous acid (Piria).—4. By solution in *nitric acid* of specific gravity 1·30 it is converted into benzo-helicin, which crystallises after standing for some time. The solution at the same time is coloured yellow by nitric peroxide (Piria):

$$C^{20}H^{22}O^{8} + O = C^{20}H^{20}O^{8} + H^{2}O.$$

Weak nitric acid acts upon populin only at the boiling heat, salicylous acid being given off from the acid solution; ordinary nitric acid acts violently, producing yellowish crystals, probably consisting of picric, nitrobenzoic and oxalic acids (Piria).—5. With strong *sulphuric acid* populin forms a deep red solution whence water throws down a red powder (Braconnot's rutilin), which, after the sulphuric acid has been removed, dissolves in water with red colour, and is reprecipitated by acids (Braconnot). Hot oil of vitriol carbonises populin. (Koninck.)

By boiling with dilute *acids*, populin is resolved into saligenin, benzoic acid and glucose:

$$\underset{\text{Populin.}}{C^{20}H^{22}O^{8}} + 2H^{2}O = \underset{\text{Saligenin.}}{C^{7}H^{8}O^{2}} + \underset{\text{Benzoic acid.}}{C^{7}H^{6}O^{2}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}};$$

and the saligenin is converted by the further action of the acid into saliretin, $C^{14}H^{12}O^{2} = 2C^{7}H^{8}O^{2} - 2H^{2}O$. Concentrated *phosphoric acid* forms saliretin even in the cold. (Braconnot.)

6. Populin heated to 100° in a sealed tube with alcoholic *ammonia*, yields salicin, benzamide and benzoic ether. Gaseous ammonia does not act on populin at 150° (Piria).—7. Heated with *potassium-hydrate*, it yields oxalate of potassium (Braconnot).—8. Populin boiled with *hydrate of calcium* or *barium* yields a benzoate and salicin:

$$\underset{\text{Populin.}}{C^{20}H^{22}O^{8}} + H^{2}O = \underset{\text{Benzoic acid.}}{C^{7}H^{6}O^{2}} + \underset{\text{Salicin.}}{C^{13}H^{18}O^{7}}.$$

100 pts. crystallised populin yield 28·9 pts. benzoic acid, the calculated quantity being 28·64 pts. (Piria).—9. By prolonged boiling with water, putrid *casein*, and carbonate of calcium, it is decomposed with formation of saligenin, lactate of calcium and benzoate of calcium. (Piria.)

Populin is not altered by *chlorine* or *iodine*, or by boiling with *phosphorus* and water (Braconnot), or by *emulsin* (Piria).

**PORCELAIN.** The finest kind of earthenware, made of the purest and whitest clay or kaolin (see Clay, i. 1024), and agglutinated by the addition of some compound such as powdered felspar, which softens and fuses at the temperature at which the ware is fired, whereby the mass is rendered semi-transparent, in the same manner as paper that has imbibed melted wax remains translucent after the latter has become fixed. The fracture of porcelain is vitreous and not earthy, and the broken surface does not adhere to the tongue like that of common earthenware; it also possesses much greater solidity and strength, and power of resisting sudden changes of temperature.

**PORCELAIN-CLAY.** See Clay (i. 1024).

**PORCELAIN, REAUMUR'S.** See Glass (ii. 844).

**PORCELAIN-SPAR.** Syn. with Scapolite.

**PORPEZITE.** The native alloy of gold and palladium (p. 326.)

**PORPHYRIC ACID.** $C^{10}H^{4}N^{2}O^{7} = C^{10}H^{4}(NO^{2})^{2}O^{3}$? (Erdmann, J. pr. Chem. xxxvii. 403.—Gm. xvii. 183.)—An acid produced by the action of nitric acid on euxanthone (ii. 610); so called from its property of producing a blood-red colour with carbonate of ammonium. A solution of euxanthone in cold nitric acid of specific gravity 1·31, becomes warm on standing, evolves red vapours, and on cooling deposits porphyric acid, which may be purified by solution in carbonate of ammonium and precipitation with hydrochloric acid. It is then obtained as a yellow, crystalline powder, or in very small reddish-yellow crystals becoming electric when rubbed.

According to the mean of Erdmann's analyses, it contains 43·63 per cent. carbon, 1·45 hydrogen, 11·82 nitrogen. The above formula, proposed by Gerhardt, which represents it as dinitro-euxanthone, requires 45·45 C, 1·51 H, 10·62 N, and 42·42 O.

Porphyric acid is slightly soluble, with red colour, in pure water, insoluble in acidulated water, very slightly soluble in cold, more soluble in boiling *alcohol*.

When boiled with *nitric acid* it yields oxypicric and oxalic acids.

The porphyrates explode when heated. The acid dissolves in carbonate of ammonium forming a blood-red *neutral ammonium-salt*, $C^{10}H^{3}(NH^{4})(NO^{2})^{2}O^{3}$, sparingly soluble with yellowish colour in water. At 130° it gives off water and ammonia, leaving a less soluble *acid salt*, which crystallises in pale red feathery crystals. The solution of this salt forms with chloride of barium, chloride of calcium, neutral acetate of lead, and nitrate of silver, red, and for the most part crystalline precipitates which dissolve in a large quantity of water. The acid ammonium-salt throws down from nitrate of silver pale orange-coloured crystalline scales. From cupric sulphate the neutral ammonium-salt precipitates black-red flocks which become granular on standing or more quickly when heated.

**Oxyporphyric acid.** This name is given by Erdmann to an acid obtained, together with oxypicric acid, by the action of boiling nitric acid on euxanthone. It forms yellow microscopic crystals, and differs from porphyric acid in forming with ammonia a salt which is more soluble in carbonate of ammonium than the porphyrate, and does not change colour from dark red to pale red when heated. The acid gives by analysis (mean) 42·76 per cent. carbon, 1·38 hydrogen, 11·95 nitrogen and 43·91 oxygen, a composition differing but little from that of porphyric acid: hence Laurent (Compt. chim. 1849, p. 384) regarded the two as probably identical.

**PORPHYRITE.** The name given by Streng to the melaphyr-porphyry (iii. 867) of the southern range of the Hartz. (For analyses see Jahresbericht, 1858, p. 769; 1861, p. 1057).

**PORPHYROXIN.** A neutral substance said by Merck to exist in some kinds of opium (p. 208). The same body is said by G. Gibb (Pharm. J. Trans. [2] i. 454) to exist in *Sanguinaria Canadensis* (see SANGUINARIA).

**PORPHYRY.** A rock consisting of a more or less compact felspathic base with crystals of felspar (often orthoclase or oligoclase) and other minerals imbedded in it. It may be green with blotches of pale green or white, or red with white blotches or specks, besides other shades of colour; the blotches of a polished surface are the felspar crystals. The name is derived from *πορφύρα*, purple, on account of the brownish or bluish-red colour of certain varieties used by the ancients for statuary. The several varieties of porphyry are named according to the nature of the crystals which occur most abundantly in them *e.g.* felspar-porphyry, quartz-porphyry &c. Eurite-porphyry has a base composed of felspar or a fine-grained mixture of felspar and quartz, enclosing crystals of various minerals. Augitic porphyry has a basaltic base enclosing crystals of augite. Granitic, syenitic, greenstone, trachyte porphyry, &c., consist of a granulo-crystalline base, intermixed with the constituents of granite, syenite, &c., and larger crystals of felspar.

**PORPOISE-OIL.** *Meerschweinthran.*—Obtained by heating the belly-blubber of the porpoise (*Delphinus Phocæna*) with water. It has a density of 0·937 at 16°, and in the fresh state, a pale yellow colour, an odour of sardines, and does not redden litmus; but on exposure to air and light, it loses its odour, becomes first darker, then nearly colourless, and acquires an acid reaction, from liberation of valerianic acid. It consists of olein, margarin [palmitin], and valerin. With 3 pts. of boiling alcohol of specific gravity 0·821, it forms a solution which becomes turbid as soon as it is removed from the fire: with 1 pt. of alcohol a more stable solution is formed, capable of taking up any further quantity of the oil. (Chevreul, *Recherches*, p. 287; Berthelot, Ann. Ch. Phys. [3] xli. 253.)

**PORPORINO.** An Italian glass resembling hæmatinone (iii. 3) in appearance, but, according to Pettenkofer, different from it in composition.

**PORTER.** See BEER (i. 529, 533).

**PORTITE.** White radiate masses from the gabbro of Tuscany, cleaving parallel to the sides of a prism of 120°. Specific gravity = 2·4. Swells up before the blowpipe, and fuses to a white enamel. Gelatinises with acids in the cold. Contains, according to Bechi (Sill. Am. J. [2] xiv. 63), 58·12 per cent. silica, 27·5 alumina, 4·87 magnesia, 1·76 lime, 0·16 soda, 0·10 potash, 7·92 water, and appears to have been formed by the decomposition of a zeolite.

**PORTLAND CEMENT.** A cement so called because it has the colour of Portland stone. It is made by mixing the argillaceous sand of the Thames with chalk. (See *Ure's Dictionary of Arts, &c.* iii. 471.)

**PORTLAND STONE.** An oolitic limestone immediately underlying the Purbeck strata; so called from its developement in the island of Portland.

**PORTUGALLO-OIL.** Essential oil of orange-peel. (See CITRUS, i. 1002.)

**POTAMOGETON.** The composition of the fennel-leaved pond-weed (*Potamogeton pectinatus*) has been determined by Hervé Margon (Jahresb. 1861, p. 735), with the following results:

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| | Combustible matter without Nitrogen. | Nitrogen. | Silica. | Lime. | Phosphoric anhydride. | Other mineral constituents. |
|---|---|---|---|---|---|---|
| *a.* | 61 8 | 2·5 | 6·0 | 12·1 | 1·0 | 16·6 |
| *b.* | 69·5 | 1·9 | 14·1 | 0·8 | . . | 13·7 |

Cloez (Compt. rend. lvii. 354; Jahresb. 1863, p. 599) finds that the gas evolved from *Potamogeton perfoliatum* under the influence of sunshine and in water continually renewed, consists wholly of oxygen and nitrogen without any trace of combustible gas, the composition varying from 46·08 per cent. oxygen in the first to 38·5 per cent. on the twentieth day. The same plant growing in ordinary aërated water slightly charged with carbonic acid, but not renewed, gave out gas also consisting wholly of oxygen and nitrogen, and containing 70·10 per cent. oxygen on the first, 87·52 on the third and 90·87 per cent. on the fifth day.

**POTASH.** This term is applied sometimes to the hydrate, sometimes to the anhydrous oxide of potassium, occasionally also to the crude carbonate; it is best however to restrict it to the hydrate, either in the solid state or in aqueous solution.

**POTASHES.** Crude carbonate of potassium, obtained by lixiviating the ashes of land-plants and boiling down the solution in iron pots.

**POTASH-LIME.** A mixture of hydrate of potassium and quicklime, prepared by evaporating a mixture of caustic potash-ley and lime in an iron pot, calcining the residue in a crucible, and rubbing it to fine powder in a warm mortar. It acts on organic bodies at high temperatures in the same manner as pure hydrate of potassium, but is more convenient, because it is less fusible and does not act so strongly on glass vessels. It is however not so much used as the analogous mixture of lime and soda.

**POTASS** or **POTASSA.** Hydrate of potassium (p. 700).

**POTASSIUM.** *Symbol* K. *Atomic Weight* 39·1.—This element is very widely diffused in nature. In the mineral kingdom it occurs as silicate, together with earthy silicates, in felspar, mica, &c.; as sulphate, combined with sulphate of aluminium, in alum stone; as chloride, bromide and iodide in sea-water and salt-deposits; and as nitrate in various soils in tropical countries. Potassium-salts enter also into the bodies of plants and animals, being taken up by plants from the soil, entering into almost every part of the vegetable structure, and being thence transferred to the animal body, where they are found as essential constituents of many organs and fluids, flesh and milk for example.

The vegetable kingdom is the chief source from which potassium-compounds are prepared. The potassium in plants exists in combination, partly with inorganic, partly with organic acids, tartaric, oxalic, citric, malic, &c.; and when a plant is burnt, the inorganic potassium-salts contained in it, the sulphate, chloride, &c., remain in the ash as such, whilst the organic salts are converted into carbonate, and from this the other salts of potassium, as well as the hydrate, or caustic potash, may be prepared. Potassium-salts are likewise obtained from the ashes of marine plants, from sea-water and brine-springs, from felspar and other potassic minerals, and from the washings of sheep's wool. (See Potassium-salts, Manufacture of.)

*Preparation of the Metal.*—Potassium was first isolated by Davy (in 1807), who obtained it by the electrolysis of the hydrate. When a piece of this substance, slightly moistened by exposure to the air, to give it sufficient conducting power, is placed on a platinum-capsule connected with the negative pole of a powerful voltaic battery (Davy used from 100 to 200 pairs of Wollaston's construction, six inches square), and touched by a platinum wire proceeding from the positive pole, it liquefies and is decomposed, globules of potassium appearing on the capsule and taking fire, unless they are quickly removed and immersed in rock-oil.

An easier method of obtaining potassium by electrolysis is that given by Matthiessen (Chem. Soc. Qu. J. viii. 30). A mixture of 1 at. chloride of potassium and 1 at. chloride of calcium (which mixture is used because it melts at a much lower temperature than chloride of potassium alone) is melted in a small porcelain crucible over a lamp, and subjected to the action of a Bunsen's battery of six elements with carbon poles, the heat being so regulated that a solid crust forms round the negative carbon pole, while the mixture remains fused and allows the free evolution of chlorine at the positive pole. When the decomposition has been continued in this manner for about twenty minutes, and the cooled crucible is opened under rock-oil, a large quantity of potassium, almost chemically pure, is generally obtained. If the same experiment be repeated at a white heat over a charcoal fire with an iron wire as negative pole, small globules of potassium are seen burning on the surface; and these are found to be almost pure. (Matthiessen.)

For preparing potassium in large quantities however, it is necessary to resort to other methods. Gay-Lussac and Thénard, soon after Davy's discovery of the metal, showed that it might be obtained in greater abundance by decomposing hydrate of potassium with metallic iron at a white heat. Iron turnings were heated to whiteness in a curved gun-barrel covered with a clay lute, and melted hydrate of potassium was allowed to pass slowly over the ignited iron. Decomposition then ensued, the iron taking up the oxygen of the hydrate, while the potassium and hydrogen were set free, the potassium passing over in the state of vapour and being condensed in a cooled copper receiver.

A still more productive method consists in decomposing carbonate of potassium with charcoal at a high temperature. This method, first suggested by Curaudau (Ann. Chim. lxvi. 97), was brought into an available form by Brunner (Bibl. Univ. xxii. 36), and has been still further improved by Maresca and Donné (Ann. Ch. Phys. [3] **xxxv.** 147). An intimate mixture of charcoal and carbonate of potassium is prepared by igniting about 6 lbs. of crude tartar (acid tartrate of potassium) in a covered iron crucible till it ceases to emit vapours. The porous mixture thus obtained is rapidly cooled by the application of cold water to the outside of the crucible, and the charred mass, broken into lumps about the size of a hazel-nut, is quickly introduced into a wrought-iron bottle (generally one of the bottles in which mercury is evaporated). The bottle is then introduced into a furnace *a* (*fig.* 739), and placed horizontally on supports of fire-brick, *f*, *f*. A wrought-iron tube *d*, four inches long, serves to convey the vapours of potassium into a receiver *e*, formed of two pieces of wrought iron, *a*, *b* (*fig.* 740), which are fitted closely to each other so as to form a shallow box only a quarter of an inch deep, and are kept together by clamp-screws. The iron plate should be ⅛th of an inch thick, 12 inches long, and 5 inches wide. The receiver is open at both ends, the socket fitting upon the neck of the iron bottle. The object of giving the receiver this flattened form is to ensure the rapid cooling of the potassium, and thus to withdraw it from the action of the carbonic oxide, which is disengaged during the entire process, and has a strong tendency to unite with the potassium, forming a dangerously explosive compound.[*] Before connecting the receiver with the tube *d*, the fire is slowly raised till the iron bottle attains a dull red heat. Powdered vitrefied borax is then sprinkled upon it, which melts and forms a coating, serving to protect the iron from oxidation. The heat is then to be urged until it is very intense, care being taken to raise it as equally as possible throughout every part of the furnace. When a full reddish-white heat is attained, vapours of potassium begin to appear and burn with a bright flame. The receiver is then adjusted to the end of the tube, which must not project more than a quarter of an inch through the iron plate forming the front wall of the furnace; otherwise the tube is liable to be obstructed by the accumulation of solid potassium, or of the explosive compound above mentioned. Should any obstruction occur, it must be removed by thrusting in an iron bar, and if this fail, the fire must be immediately withdrawn by removing the bars from the furnace, with the exception of two which support the iron bottle. The receiver is kept cool by the application of a wet cloth to its outside. When the operation is complete, the receiver with the potassium is removed and immediately plunged into a vessel of rectified Persian naphtha provided with a cover, and kept cool by immersion in water. When the apparatus is sufficiently cooled, the potassium is detached and preserved under naphtha.

*Fig.* 739.

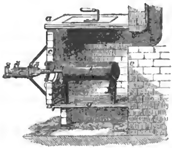
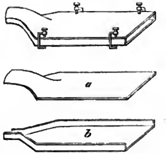


*Fig.* 740.



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[*] In Brunner's original process, copper receivers were used of cylindrical form and much larger dimensions than those above described (see Graham's *Elements of Chemistry*, 2nd ed. i. 521). But with these receivers the condensation of the potassium is found to be very uncertain; and when the iron connecting tube is kept red-hot throughout its whole length, as it should be to prevent obstruction, the whole of the metal sometimes escapes in the form of vapour, not a particle condensing in the receiver. (**Maresca** and **Donné**.)

To obtain the maximum produce of potassium, it is necessary that the mixture of potassic carbonate and charcoal should contain 1 at. of the carbonate to 2 at. carbon, such a mixture when heated being wholly converted into potassium and carbonic oxide:

$$K^2CO^3 + C^2 = K^2 + 3CO.$$

To ascertain whether this is the case, the burnt tartar must be analysed, and any deviation from the required proportions must be rectified by mixing samples of tartar of different qualities. But even when the right proportions are attained, the quantity of crude potassium obtained does not exceed one-fourth of the weight of the charge, whereas if the process could be carried on without loss, the yield should be about one-half, as 162 pts. of the mixture of carbonate and charcoal contain 78 pts. of potassium. Kühnemann (Jahresb. 1864, p. 180) recommends the addition of chalk to the burnt tartar, in such proportion that the mixture may contain 100 pts. potassic carbonate to 20 pts. carbon and 13·5 to 14 pts. calcic carbonate.

The potassium obtained by this process is not pure, but always contaminated with compounds containing carbon and oxygen. To remove these, it must be distilled a second time in an iron retort, and this precaution is essential, as if the crude potassium is exposed to the air, and even if it is preserved under naphtha, a black detonating compound is quickly formed, which explodes violently on the slightest friction. The purified metal amounts to about two-thirds of the quantity operated on. A third distillation may be necessary if the potassium is required to be perfectly pure. A little impure potassium always remains in the tube attached to the retort; and to prevent the possibility of its forming the detonating compound above mentioned, the tube should be detached as soon as it is cold and immersed in water.

*Properties.*—Potassium is a bluish-white metal of specific gravity 0·865, being the lightest of all the metals except lithium, and capable of floating easily on water. At 0° it is brittle and has a crystalline fracture; it becomes malleable at a slightly higher temperature, soft at 15°, pasty at a few degrees higher, and completely fluid at 62·5°. In the soft state it may be cut with a knife, and two clean surfaces of the metal may be welded together like white-hot iron. At a red heat it may be distilled, yielding a beautiful green vapour. When freshly cut it possesses considerable lustre, but instantly tarnishes from oxidation when exposed to the air; indeed it is so greedy of oxygen that it can only be preserved in the metallic state by immersing it in mineral naphtha or enclosing it in a sealed tube. When a few grammes of the metal are melted in a sealed tube filled with coal-gas, then left to cool till a few solid points appear on the surface, the remaining liquid portion poured off by suddenly inclining the tube, the solidified portion remains in shining octahedral crystals belonging to the dimetric system, and having the angle P : P = 52° in the terminal, and about 76° in the basal edges. (C. E. Long, Chem. Soc. Qu. J. xiii. 122.)

Potassium when heated in the *air* to its point of volatilisation, bursts into flame and burns rapidly with a violet light. When thrown upon *water*, it decomposes the water with great violence, displacing half the hydrogen and forming hydrate of potassium:

$$2H^2O + K^2 = 2KHO + H^2.$$

The escaping hydrogen carries with it a small portion of the volatilised metal, and takes fire from the heat evolved, burning with a beautiful rose-red flame, while the melted metal floats about on the water, and finally disappears with an explosive burst of steam as the globule of melted potash becomes cool enough to come into contact with the water. Potassium likewise decomposes nearly all gases containing *oxygen*, when heated in contact with them; and at high temperatures removes oxygen from almost all bodies containing that element. On the other hand it is separated from its hydrated oxide when very strongly heated in contact with iron or charcoal, the decomposition being doubtless greatly facilitated by the volatility of the potassium. (See CHEMICAL AFFINITY, i. 859.)

Potassium absorbs *hydrogen* at a heat short of redness, and is converted into a greyish hydride (perhaps $HK^4$), from which however the hydrogen is expelled at a stronger heat.—Potassium unites directly with *chlorine*, *bromine*, *iodine*, *sulphur*, *selenium* and *tellurium*, burning vividly when heated in contact with them.—It also combines with *phosphorus*, the combination being attended with evolution of light and heat when the two bodies are heated together in nitrogen gas; under mineral naphtha it takes place without visible combustion.—When moderately heated in *carbonic oxide gas*, or when its vapour is allowed to condense slowly in an atmosphere of that gas, it absorbs the carbonic oxide, forming the black mass above mentioned (p. 693), from which the metal cannot be recovered.

Potassium is a monatomic metal, belonging to the group which includes the other alkali-metals, cæsium, rubidium, lithium, and sodium, together with silver. With chlorine, bromine, iodine and fluorine, it forms the compounds KCl, KBr, &c.; with chlorine also a subchloride, $K^2Cl$; with oxygen it forms a protoxide, $K^2O$, the corresponding hydrate, KHO, a dioxide, $K^2O^2$, and a tetroxide, $K^2O^4$; with sulphur, a protosulphide, $K^2S$, a sulphydrate, KHS, and several polysulphides.

**POTASSIUM, ALLOYS OF.** Potassium forms alloys with most other metals, the combination being generally effected by fusing the two metals together. Antimonide, arsenide and bismuthide of potassium are produced either in this manner or by heating the respective metals with cream of tartar. These compounds, when distilled with the alcoholic iodides, yield the arsenide, &c., of the corresponding alcohol-radicles (i. 339, 397, 596). The arsenide and antimonide decompose water, with evolution of arsenetted and antimonetted hydrogen.

An alloy of potassium and sodium containing 76·5 per cent. of the former, is produced by heating hydrate of potassium with sodium in a tube containing caoutchin to the boiling point of the liquid. It is fluid at ordinary temperatures and takes fire in contact with water (Gr. Williams, Rép. Chim. pure, iii. 177). Wanklyn (*loc. cit.*) obtained an alloy of these metals, also liquid at ordinary temperatures, by heating acetate of potassium with sodium.

The other alloys of potassium, some of which are described under the respective metals, are of no particular importance. Respecting the amalgam of potassium, see Mercury (iii. 889).

**POTASSIUM, AMIDES OF.** *Monopotassamide*, $KH^2N$, is formed when potassium is gently heated in ammonia-gas. It is an olive-green substance, exhibiting a brown colour by transmitted light when in very thin scales; is a non-conductor of electricity, melts at a little above 100°, and when heated in a close vessel, is resolved, at a temperature a little below redness, into ammonia and tripotassamide: $3KH^2N = 2H^3N + K^3N$. At a dull red heat the ammonia is partly resolved into hydrogen and nitrogen. When heated to fusion in the *air* or in *oxygen gas*, it burns rapidly and is converted into hydrate of potassium, with evolution of nitrogen. With *water* it forms ammonia and hydrate of potassium:

$$KH^2N + H^2O = H^3N + HKO.$$

Acids and alcohols act upon it in a similar manner (Gay-Lussac and Thénard, *Recherches physico-chimiques*, i. 337; H. Davy, Phil. Trans. 1809, pp. 40 and 450). With *anhydrous alcohol* it yields ammonia and ethylate of potassium:

$$KH^2N + C^2H^5.H.O = H^3N + C^2H^5.K.O.$$

Similarly with *phenol*. When warmed with an ethereal solution of *acetic anhydride*, it forms acetamide and acetate of potassium:

$$(C^2H^3O)^2O + KH^2N = \left.\begin{matrix}C^2H^3O\\H^2\end{matrix}\right\}N + \left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O.$$

*Lactide* dissolved in ether acts slowly on it, ammonia being set free and lactate of potassium formed. An ethereal solution of *succinic anhydride* has no action upon it. With compound ethers it yields ammonia and resinous products; with *benzoate* and *acetate of ethyl* it yields also the corresponding potassium-salts; with *oxalate of ethyl* it forms oxalate and oxamate of potassium. Sulphate of ethyl and oxalate of methyl do not act upon it. With *chloride of benzoyl* dissolved in anhydrous ether it forms benzamide and dibenzamide, according to the equation:

$$3C^7H^5OCl + 3KH^2N = \left.\begin{matrix}C^7H^5O\\H^2\end{matrix}\right\}N + \left.\begin{matrix}(C^7H^5O)^2\\H\end{matrix}\right\}N + 3KCl + H^3N.$$

When the amide is brought into direct contact with chloride of benzoyl without the intervention of ether, a very violent action takes place, sometimes attended with inflammation, and a number of secondary products are formed, including hydrochloric acid, benzoic acid and benzoic cyanide. (Baumert and Landolt, Ann. Ch. Pharm. cxi. 1; Jahresb. 1859, p. 125.)

*Tripotassamide* or *Nitride of Potassium*, $K^3N$, obtained by heating monopotassamide without access of air, is a greenish-black infusible substance, which, when very strongly heated without access of air, is resolved into potassium and nitrogen. On exposure to the *air*, it generally takes fire spontaneously, burning with a dark-red flame. With *water* it effervesces violently, yielding ammonia and hydrate of potassium; $K^3N + 3H^2O = H^3N + 3KHO$. It unites with *sulphur* or *phosphorus* when heated, forming a highly inflammable mixture, which in contact with water gives off sulphydric acid or phosphoretted hydrogen as well as ammonia. (Gay-Lussac and Thénard, Davy.)

**POTASSIUM, ANTIMONIDE OF.** See Antimony (i. 317).

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**POTASSIUM, ARSENIDE OF.** See Potassium, Alloys of (p. 695). The compound $K^3As$ is formed by heating potassium in arsenetted hydrogen. It is a chestnut-brown powder, which is decomposed by water, giving off arsenetted hydrogen, and forming hydrate of potassium; $K^3As + 3H^2O = H^3As + 3KHO$. Alloys containing larger proportions of arsenic likewise yield solid arsenide of hydrogen (i. 371).

**POTASSIUM, BORIDE OF?** Potassium and boron when heated together, unite without inflammation, forming a grey metallic mass, which conducts electricity, and is decomposed by contact with water, yielding potash and hydride of boron (Davy). According to Gay-Lussac and Thénard, the product obtained as above is only a mechanical mixture of boron and potassium.

**POTASSIUM, BROMIDE OF.** KBr.—Potassium and bromine unite directly, with violent inflammation and detonation. The bromide is also formed by heating potassium in hydrobromic acid gas, and by the action of bromine on fused iodide of potassium. It may be prepared: 1. By neutralising hydrobromic acid with potash.—2. By decomposing bromide of iron with an equivalent quantity of potassic carbonate.—3. Together with the bromate, by adding bromine to a solution of caustic potash till the liquid acquires a slight permanent yellow colour. The bromate may then be decomposed by passing a current of sulphydric acid through the solution, the excess of the gas expelled by gentle heating, the liquid filtered from the deposited sulphur, and evaporated till it yields crystals of the bromide (Löwig).—F. Klein (Ann. Ch. Pharm. cxxviii. 237) prepares the salt by decomposing bromide of calcium (obtained by triturating 1 pt. amorphous phosphorus with 12·5 pts. bromine and water, and slightly supersaturating the resulting aqueous hydrobromic acid with milk of lime) with sulphate of potassium (13 pts.), leaving the mixture to itself for 12 hours, then evaporating the filtrate and wash-water, adding carbonate of potassium as long as turbidity ensues, and evaporating the filtered liquid to the crystallising point.

Bromide of potassium crystallises in very brilliant cubes, sometimes elongated into prisms or flattened to plates. It has a specific gravity of 2·690 (Schröder, Jahresb. 1859, p. 12); tastes sharp; decrepitates in the fire, and melts without decomposition. It dissolves more abundantly in hot than in cold *water*, and is slightly soluble in *alcohol*. It is decomposed at a red heat by *chlorine*. With aqueous *hypochlorous acid*, it yields bromate and chloride of potassium, bromine and chlorine being set free. When fused with *chlorate of potassium*, it is converted into bromate. According to Hempel (Ann. Ch. Pharm. cvii. 160), it is not decomposed in neutral solution by *permanganate of potassium*, even at the boiling heat; but on addition of sulphuric acid, bromine is set free even in the cold, and after boiling for a few minutes the decomposition is complete, the liquid no longer containing any bromine.

**POTASSIUM, CARBIDE OF?** Charcoal which has been heated to redness in contact with potassium, effervesces afterwards in contact with water: hence the charcoal appears to have taken up a portion of the potassium, as the metal, if heated alone, would volatilise entirely. (Davy.)

**POTASSIUM, CARBOXIDE OF.** KCO.—Potassium unites directly with carbonic oxide, as first observed by Liebig (Ann. Ch. Pharm. xi. 182). According to Brodie (Chem. Soc. Qu. J. xii. 269), pure potassium heated to about 80° in carbonic oxide free from air, is at first slowly converted into an arborescent group of dull grey crystals; but if the passage of the gas be further continued, a more rapid absorption takes place, even at a lower temperature, and the grey crystals are converted into a dark red compound $K^2C^2O^2$. The grey substance, which cannot be obtained pure, appears to consist of $K^2CO$. The dark red compound may be preserved under mineral naphtha, but is decomposed with extreme violence by water, and even in the dry state, sometimes explodes from causes which have not been made out. On carefully adding it to anhydrous alcohol, great heat is evolved, part of the substance, containing $\frac{2}{5}$ths of the entire quantity of potassium, dissolves, without evolution of gas, and the rest separates as rhodizonate of potassium, probably thus:

$$\underset{\text{Carboxide of Potassium.}}{5K^2C^2O^2} = 2K^2O + \underset{\text{Rhodizonate of Potassium.}}{K^6C^{10}O^8}.$$

Hence the carboxide may be regarded as a compound of protoxide and rhodizonate, or as a basic rhodizonate of potassium (see Rhodizonic Acid).

The black explosive substance formed in the preparation of potassium, by heating carbonate of potassium with charcoal, appears to consist of one or both of the compounds just described. According to Kühnemann (Jahresb. 1864, p. 180), when potassium is intensely heated in carbonic oxide gas, there are formed: first, a grey mixture of oxide of potassium and free carbon, which separates as the apparatus cools from a white to a red heat; and secondly a black red body, which separates at a temperature below dull redness, both compounds being formed without access of water or moist air. When the vapours which escape from the receiver in the preparation of potassium are passed, first into a bottle partly filled with naphtha, and thence into an empty bottle, the grey substance collects chiefly in the first bottle, the red in the second, part of it however escaping uncondensed, and imparting a red colour to water into which it is passed. The red substance dissolves in water without evolution of gas, forming a solution which exhibits all the reactions of rhodizonate of potassium. The explosion of the grey substance is attributed by Kühnemann either to the heating of the mass by absorption of water, or to the formation of peroxide of potassium (from the protoxide present) and its action on the free carbon.

**POTASSIUM, CHLORIDE OF.** KCl. *Digestive Salt. Sal digestivum. Sylvii. Sal febrifugum Sylvii.*—Potassium takes fire in chlorine gas at ordinary temperatures, burning with a red flame and producing chloride of potassium. This salt is also formed by passing chlorine over red-hot hydrate or iodide of potassium; by gently heating potassium in hydrochloric acid gas; by dissolving hydrate or carbonate of potassium in aqueous hydrochloric acid; and by the action of potassium on fused chloride of magnesium and other metallic chlorides. It occurs native, sometimes pure but more abundantly mixed or combined with other chlorides. Pure chloride of potassium, or *sylvine*, is found in cubic crystals about the fumaroles of Vesuvius, also in thin layers in the salt-beds of Stassfurth near Magdeburg. In the same locality there occurs above the rock-salt, a deposit of chloride of potassium and magnesium, or *carnallite*, $KCl.Mg''Cl^2.6H^2O$, forming a layer between 60 and 70 feet thick, interspersed with layers of rock-salt and kieserite, $Mg''SO^4.H^2O$. This deposit is worked for the extraction of the potassium-chloride. On dissolving the carnallite in warm water, and leaving the solution to cool, the greater part of the chloride of potassium separates out, while the whole of the chloride of magnesium remains in solution. The method of recovering the remainder of the potassium-chloride from the mother-liquor, will be described hereafter (p. 718). Chloride of potassium occurs also with the chlorides of sodium, magnesium, calcium, and other salts, in sea-water and brine-springs, and is obtained as a bye-product in the preparation of chlorate of potassium, the purification of saltpetre, and in several other manufacturing operations (see POTASSIUM-SALTS, MANUFACTURE OF, p. 716).

Chloride of potassium crystallises in cubes often prismatically elongated; rarely (from solution containing free potash) in octahedrons. Specific gravity = 1·836 (Kirwan), 1·9153 (Karsten), 1·945 (Kopp), 1·998 (Schröder), 1·986 (Schiff). It tastes like common salt; is not acted on by the air; decrepitates when heated; melts at a low red heat; volatilises unchanged at a higher temperature. It is somewhat more volatile than chloride of sodium; in a covered crucible it may be kept in a state of fusion without loss; but in open vessels it volatilises gradually in the constantly renewed current of air. (H. Rose.)

Chloride of potassium is more soluble in *water* than common salt, and produces a much greater degree of cold in dissolving than the latter, but less than sal-ammoniac. One part dissolves at 17·5° in 3·008 parts of water, forming a solution of specific gravity 1·1635 (Karsten): it dissolves at 11·8° in 2·89 parts, at 13·8° in 2·87 parts, and at 15·6°, in 2·85 parts of water (Kopp); 100 parts of water at 0° dissolve 29·23 parts of chloride of potassium, and for every degree above, 0·2738 parts (Gay-Lussac).

Solutions containing various percentages of chloride of potassium have the following specific gravities: According to Schiff (Ann. Ch. Pharm. cvii. 293; Jahresb. 1859, p. 39):

| Percentage | 2·75 | 5·50 | 8·25 | 11·00 | 16·50 | 24·75 |
|---|---|---|---|---|---|---|
| Specific gravity at 15° | 1·017 | 1·0360 | 1·0529 | 1·0730 | 1·1115 | 1·1729 |

According to Gerlach (Jahresb. 1859, p. 43):

| Percentage | 5 | 10 | 15 | 20 | 24·9 |
|---|---|---|---|---|---|
| Specific gravity at 15° | 1·0325 | 1·0651 | 1·1004 | 1·1361 | 1·1733 |

Respecting the expansion by heat of solutions of potassium-chloride of various strengths, see Kremers (Pogg. Ann. Ch. Pharm. 394; Jahresb. 1857, p. 68); respecting the tension of aqueous vapours given off from its solutions, see Wüllner (Pogg. Ann. ciii. 529; Jahresb. 1859, p. 44).

Chloride of potassium is but slightly soluble in strong *alcohol*. According to Schiff (Ann. Ch. Pharm. cxviii. 362; Jahresb. 1861, p. 87), 100 pts. of spirit of various strengths are capable of dissolving at 15°, the following quantities of potassium-chloride:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Quantity of absolute alcohol in 100 pts. of spirit. | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 80 |
| Quantity of KCl in 100 pts. of saturated solution. | 24·6 | 19·8 | 14·7 | 10·7 | 7·7 | 5·0 | 2·8 | 0·45 |

100 pts. of wood-spirit containing 40 per cent. methylic alcohol are capable of dissolving, at the same temperature, 9·2 pts. of potassium-chloride.

Chloride of potassium is decomposed by *sulphuric*, *nitric* or *tartaric acid*, with separation of hydrochloric acid and formation of sulphate, &c. of potassium. According to Baumhauer (Jahresb. 1859, p. 128), 1 at. chloride of potassium in aqueous solution is completely converted into nitrate by 2 at. nitric acid.

Chloride of potassium absorbs the vapour of *sulphuric anhydride*, forming a hard translucent mass consisting of $KCl.SO^3$ or $\left.\begin{matrix}(SO^2)''\\ K\end{matrix}\right\}\begin{matrix}O\\ Cl\end{matrix}$ (analogous to Williamson's chlorhydrosulphuric acid $\left.\begin{matrix}(SO^2)''\\ H\end{matrix}\right\}\begin{matrix}O\\ Cl\end{matrix}$), which is instantly decomposed by water. With *chromic anhydride* it forms a similar compound $KCl.CrO^3$, which is also decomposed by water; it is obtained in needles when a solution of acid potassium-chromate in hydrochloric acid is allowed to crystallise.

Chloride of potassium unites with most other metallic chlorides, forming crystallisable double salts; these are described with the chlorides of the several metals. *Chloride of potassium and magnesium* occurs, as already observed, in the salt deposit of Stassfurth (see also POTASSIUM-SALTS, MANUFACTURE OF, p. 717).—*Kremersite*, a mineral occurring in red octahedrons about the fumaroles of Vesuvius, consists of chloride of potassium mixed or combined with the chlorides of sodium, ammonium and iron.

*Hemichloride* or *Subchloride of Potassium*, $K^2Cl$.—Produced by melting the ordinary chloride with potassium in a stream of hydrogen. It is a dark blue compound, which is decomposed by water, with evolution of hydrogen and formation of potassic chloride and hydrate:

$$K^2Cl \quad + \quad H^2O \quad = \quad KCl \quad + \quad KHO \quad + \quad H$$

(H. Rose, Pogg. Ann. cxx. 1). A blue compound, probably identical with the above, is formed when potassium is heated with chloride of phenyl.

**POTASSIUM, CYANIDE OF.** See CYANIDES (ii. 268).

**POTASSIUM, DETECTION AND ESTIMATION OF.** 1. *Reactions in the dry way.*—Potassium-compounds impart a violet colour to the outer blowpipe flame. Alcoholic solutions of potassium-salts burn with a violet flame. The colour is not perceptible to the naked eye in presence of sodium (or lithium); but if a thick plate of dark blue glass be interposed between the eye and the flame, the yellow sodium flame is completely cut off, and the potassium-flame then becomes distinctly visible, of a rich reddish-violet colour. In this manner a very small quantity of potassium may be detected in presence of a large amount of sodium. In the spectroscope, potassium-salts exhibit a spectrum very much like the ordinary solar spectrum, but characterised by a bright line near the red, and a fainter line near the violet extremity.

The normal sulphate, carbonate, phosphate, arsenate and borate of potassium, are not decomposed by heat. The chloride, bromide, iodide and hydrate volatilise without decomposition at very high temperatures. Most other potassium-salts are decomposed by heat.

2. *Reactions in Solution.*—All potassium-salts are soluble in water, and most of them easily soluble. The normal potassium-salts of strong acids, *e.g.* $KCl$, $KNO^3$, $K^2SO^4$, $C^2K^2O^4$, &c., are neutral to test-paper, and the corresponding acid salts, *e.g.* $KHSO^4$, $CHKO^4$, &c., have an acid reaction; but in the case of the weaker acids, the alkaline reaction of the potash predominates in the normal, and even in the acid salts; thus the normal and acid carbonates, $K^2CO^3$ and $KCHO^3$, have an alkaline reaction; so likewise have all the borates, excepting the pentaborate, $KH^4B^5O^{10}$, which is neutral (i. 645).

Solutions of potassium-salts, if not too dilute, form with *platinic chloride* a yellow crystalline precipitate of chloroplatinate of potassium, $K^2PtCl^6$, slightly soluble in water, insoluble in alcohol and in acids. If very little potassium be present, the solution must be saturated with hydrochloric acid, platinic chloride added, the whole evaporated to dryness, and the residue treated with alcohol, which leaves the chloroplatinate undissolved.

Concentrated potassium-solutions form with *tartaric acid* (or better, with acid *tartrate of sodium*) a white crystalline precipitate of acid tartrate of potassium, soluble in about 180 pts. of cold water, readily soluble in acids or in alkaline solutions, insoluble in alcohol. In dilute aqueous solutions, the formation of the precipitate is greatly facilitated by addition of alcohol, also by agitating the solution or scratching the sides of the test-tube with a glass rod.

*Hydrofluosilicic acid* forms in solutions of potassium-salts, a white, gelatinous precipitate of potassic silicofluoride.—*Perchloric acid* forms a precipitate of perchlorate, insoluble in alcohol. When a concentrated solution of *aluminium-sulphate* is added to a concentrated solution of a potassium-salt, octahedral crystals of alum are deposited on evaporating the solution.

In mixed solutions, potassium must be looked for in the liquid which remains after the removal of all the metals which are precipitable by sulphydric acid, sulphide of ammonium, and carbonate of ammonium, and of magnesium by baryta-water. It may then be detected by its reactions with platinic chloride and tartaric acid; also by evaporating the solution to dryness, and examining the colour and spectrum of the flame as above described.

3. *Estimation and Separation.*—Potassium, when it occurs in a compound not containing any other metal or any fixed acid, may be estimated directly either as sulphate or as chloride. All potassium-salts containing volatile acids are decomposed by heating them with sulphuric acid, the excess of which may afterwards be expelled by a stronger heat, and the quantity of potassium or potash calculated from the weight of the residual neutral sulphate. It is difficult, however, to expel the last traces of free sulphuric acid by mere ignition; but they may be completely driven off by dropping a lump of carbonate of ammonia into the crucible, and repeating the ignition with the cover on; the sulphuric acid then diffuses into the atmosphere of ammonia in the crucible, and a perfectly neutral sulphate remains, containing 41·52 per cent. potassium, or 54·06 per cent. of potassic oxide, $K^2O$.

In estimating potassium as chloride, the only precaution to be observed, is to ignite the chloride in a covered crucible, as, when strongly heated in contact with the air, a portion of it volatilises. The chloride contains 52·4 per cent. potassium, equivalent to 63·19 $K^2O$.

The separation of potassium from all metals, excepting the other alkali-metals, is effected by the reagents above mentioned. From sodium and lithium it is separated by *chloride of platinum*, adding alcohol to complete the precipitation of the chloroplatinate of potassium. The precipitate is then collected on a weighed filter, washed with alcohol and dried at 100°. It contains 16·04 per cent. potassium, equivalent to 19·31 $K^2O$.

Precipitation with chloride of platinum serves also to separate potassium from all other metals which do not form insoluble chlorides, and from all non-metallic elements.

From cæsium and rubidium, potassium may be separated by the greater solubility of its chloroplatinate in water (i. 1114), or according to Redtenbacher (Bull. Soc. Chim. 1865, ii. 201), by the difference of solubility of the alums of the three metals, 100 pts. water at 17° dissolving 13·5 pts. of potassium-alum, but only 2·27 pts. of rubidium-alum and 0·619 pts. of cæsium-alum.

The amount of hydrate or of carbonate of potassium in a solution not containing any other alkali, or in commercial potashes, may be estimated by alkalimetry (i. 117, 263), and the same method may be applied to the commercial valuation of organic potassium-salts, tartars for example, after they have been converted into carbonate by ignition.

For the estimation of potassium in silicates, see SILICATES.

4. *Atomic Weight of Potassium.*—The method of determining the atomic weight of this element, in connection with those of chlorine and silver, has been already described under CHLORINE (i. 905). The experiments of Marignac give K = 39·12; those of Stas give K = 39·14.

**POTASSIUM, FLUORIDE OF.** KF.—Produced by dissolving potassium or the hydrate or carbonate in hydrofluoric acid, evaporating, and heating strongly to expel the excess of acid. It is deliquescent, very soluble in water, and crystallises from an aqueous solution evaporated under 40°, in colourless cubes often lengthened into prisms, or exhibiting square, pyramidally excavated faces. Specific gravity = 2·454 (Bödeker). It melts below a red heat, has a sharp, saline taste and alkaline reaction, and is decomposed by strong sulphuric acid, even at ordinary temperatures. It is insoluble in alcohol, and is precipitated thereby from the aqueous solution in long, thread-like, radiating crystals containing $KF.2H^2O$. (H. Rose, Pogg. Ann. lv. 554.)

Fluoride of potassium forms definite crystallisable compounds with many other fluorides. The *fluoride of boron and potassium*, $KBF^4$, has been already described (i. 634). *Silico-fluoride of potassium* will be described under SILICIUM.

*Fluoride of Potassium and Hydrogen*, $KHF^2$ or KF.HF, is obtained by leaving a solution of potassium-fluoride containing excess of hydrofluoric acid to evaporate in a platinum-dish, in rectangular four-sided tables with truncated lateral edges, or by very slow evaporation in a deeper vessel, in cubes (Berzelius). According to

Marignac (Phil. Mag. [4] xv. 157), it forms quadratic tables. W. Gibbs (Bull. Soc. Chim. 1865, ii. 359) recommends this salt as a convenient reagent for decomposing refractory silicates and other minerals; beryl, columbite, chrome-iron, and cassiterite, are easily disintegrated and decomposed by fusion with it.

The compounds of potassium-fluoride with the fluorides of other metals are described under the several metals.

**POTASSIUM, HYDRATE OF.** KHO or $K^2O.H^2O$. *Potash. Caustic Potash. Potassa. Vegetable Alkali. Pflanzenlaugensalz.*—This compound may be produced by dissolving anhydrous protoxide of potassium, $K^2O$, or the peroxide, $K^2O^4$, in water, the excess of oxygen being given off in the latter case. This indeed appears to be the only means of obtaining the hydrate absolutely pure. But it is generally prepared for use by decomposing carbonate of potassium in dilute solution with slaked lime. In an iron vessel provided with a closely-fitting cover, 1 pt. of carbonate of potassium is heated with 12 pts. of water till it boils; and slaked lime—prepared by mixing 2 pts. of quicklime with 9 pts. of warm water, and keeping it in a covered pan till it is reduced to a soft powder—is then added by degrees. After each addition of lime, the mixture is boiled for a few minutes in order that the carbonate of calcium may become dense, and fall readily to the bottom. When all the lime has been added, the whole is boiled for a quarter of an hour, with the cover on, and left for the lime, &c. to settle down. The caustic solution—which should no longer effervesce when poured into hydrochloric acid, or give any, or very little cloudiness with lime water (if otherwise, longer boiling, and perhaps, also, an addition of milk of lime, is requisite)—is then drawn off into stoppered bottles by a siphon first filled with water. The residue is once or twice boiled for half an hour with a small quantity of water, and the remaining portion of potash separated by subsidence and decantation. The rest of the lime is deposited in the stoppered bottles. The decanted solution is first rapidly concentrated in covered iron pots; and if it becomes turbid, set aside in stoppered vessels, and then decanted; and lastly, rapidly boiled down in a silver basin, till the oily hydrate which remains begins to evaporate as a whole in white clouds.

To ensure the complete separation of the carbonic acid from the potash, it is necessary to use a considerable quantity of water. When only 4 pts. of water are used to 1 pt. carbonate of potassium, no decomposition takes place; and a concentrated solution of caustic potash withdraws the acid from carbonate of calcium (Liebig). The lime may also be mixed with the solution of potassic carbonate at ordinary temperatures, and the liquid set aside in stoppered vessels; but then the decomposition proceeds more slowly, and frequent shaking is required; the carbonate of calcium is also less dense than when the liquid is boiled, and consequently the decantation is more difficult. Moreover carbonate of potassium almost always contains silica, which is not precipitated at ordinary temperatures, but completely by sufficient boiling; for it then forms an insoluble compound with the excess of lime and the potash. Any alumina that may be present is separated in the same way. As the alkaline solution absorbs carbonic acid from the atmosphere very greedily, the air must be kept from it as much as possible. A portion of carbonic acid is always reabsorbed during evaporation, unless this process is performed in a silver vessel fitted with a head. When the caustic solution is evaporated down to an oily consistence, the greater part of the carbonate separates in solid particles, which float on the surface, and can then be taken off by means of a spatula. If crude potash or pearl-ash is used instead of pure carbonate of potassium, the hydrate of potassium produced contains the chloride and sulphate present in the original substance. Hence, to obtain pure hydrate of potassium, it is best to use the pure neutral carbonate obtained by igniting cream of tartar, or the crystallised acid carbonate, and decompose it with lime obtained by igniting black marble.

According to Berthollet's plan, however, tolerably pure hydrate of potassium—the *Potasse à l'alcool*—may be obtained from impure carbonate. The caustic solution. obtained as above, is evaporated to the thickness of syrup, shaken in close vessels with one-third of its volume of alcohol, and the mixture left to settle. Two strata are thereby formed, the lower of which is an aqueous solution of chloride, carbonate, and sulphate of potassium, together with a portion of caustic potash, and rests on a precipitate which may contain lime, oxide of iron, and sulphate of potassium, while the upper stratum is a solution of caustic potash with some chloride of potassium in alcohol. This is poured off, and freed from the greater part of the spirit, by distillation in a silver vessel furnished with a still-head, and boiled down in a silver basin till the hydrate begins to sublime. The resinous matter produced by the decomposition of the alcohol, and found floating on the surface, is then removed, and the hydrate is poured out on plates. It is free from sulphate of potassium, but contains chloride, and traces of carbonate and acetate.

Pure hydrate of potassium may also be prepared: *a.* By decomposing the sulphate with baryta-water, added in just sufficient quantity, or better in slight excess, as on

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evaporating the decanted solution, the small excess of baryta is precipitated by the carbonic acid of the air. (Schubert, J. pr. Chem. xxvi. 117.)

*β*. By decomposing pure nitrate of potassium with metallic copper at a red-heat: 1 pt. of saltpetre and 2 or 3 pts. of thin copper plate cut into small pieces, are arranged in alternate thin layers in a covered copper crucible, and exposed for half an hour to a moderate red-heat. The cooled mass is then treated with water, the liquid left to stand in a tall covered cylindrical vessel till the oxide of copper has completely settled down, and the pure solution of potash is then decanted with a siphon. With the above proportions of saltpetre and copper, part of the latter is converted only into suboxide. It may, therefore, be used for a second preparation of potash by mixing 1 pt. of it with 1 pt. of saltpetre and 1 pt. of metallic copper. Iron may also be used to decompose the saltpetre; but the potash thereby obtained is contaminated with small quantities of carbonic acid, silica, &c. (Wöhler, Ann. Ch. Pharm. lxxxvii. 373.)

F. Schulze (Zeitschr. Ch. Pharm. 1861, p. 109) heats a mixture of 1 pt. pure nitrate of potassium and 1 pt. pure ferric oxide (prepared from ferrous oxalate) to low redness in a covered copper crucible into which hydrogen gas is passed by a tube reaching nearly to the bottom. The nitric acid is easily decomposed, and at the end of the experiment the potash is found mixed with the ferric oxide, from which it may be dissolved out by water.

Hydrate of potassium prepared by the ordinary method from the carbonate may contain the following impurities:—*Carbonate of calcium*, originating from imperfect decantation.—*Oxide of iron*, when the caustic solution is evaporated in an iron vessel to such an extent that it begins to act upon the iron. These, together with other insoluble substances accidentally present, remain behind when the potash is dissolved in water.—*Peroxide of potassium*. Formed in small quantity, towards the end of the evaporation, when conducted in the air. It is owing to the presence of this substance that the hydrate, when dissolved in water, gives off oxygen gas.—*Carbonate of potassium*. The solution effervesces with acids.—*Sulphate of potassium*.—Chloride of barium, with excess of dilute hydrochloric acid, gives a precipitate.—*Chloride of potassium*. A precipitate produced even when the liquid is very dilute, with a solution of silver, nitric acid being added in excess.—*Nitrate of potassium*. Gives the reactions of the nitrates (p. 83).—*A few oxides of the heavy metals*. The solution, supersaturated with acetic acid, gives a precipitate with sulphydric acid or sulphide of ammonium.

*Properties*.—Hydrate of potassium, after fusion, is a white, hard, brittle substance, having a specific gravity of 2·1 (Dalton), and often a fibrous texture. It melts below redness, forming an oily liquid clear as water, and volatilises at a full red heat in white pungent vapours. It rapidly absorbs moisture and carbonic acid from the air; dissolves in about half its weight of water, evolving great heat, and is almost equally soluble in alcohol. It has a peculiar nauseous odour, and an acrid taste, and acts as a powerful cautery, quickly destroying both animal and vegetable matters: hence its solution cannot be filtered except through glass or sand, and is always best clarified by subsidence and decantation. The solution should be kept in glass bottles free from lead, as it gradually corrodes lead-glass, dissolving out the oxide of lead. It also attacks vessels of green glass or porcelain when heated in them.

A hot concentrated solution of caustic potash deposits on cooling, transparent, colourless, very acute rhombohedrons of a hydrate containing $KHO.2H^2O$ or $K^2O.5H^2O$.

The following tables give approximately the proportion of potassic oxide, $K^2O$, contained in 100 pts. by weight of solutions of different densities.

| Dalton (*System*, ii. 293). | | | Tünnermann (N. Tr. xviii. 2, 5; at 15°). | | | |
|---|---|---|---|---|---|---|
| Specific gravity. | $K^2O$ per cent. | Boiling point. | Specific gravity. | $K^2O$ per cent. | Specific gravity. | $K^2O$ per cent. |
| 2·40 | 39·9 | 129·5° | 1·3300 | 28·290 | 1·1437 | 14·145 |
| | | | 1·3131 | 27·158 | 1·1308 | 13·013 |
| 2·20 | 36·8 | 123·9 | 1·2966 | 26·027 | 1·1182 | 11·882 |
| 1·42 | 34·4 | 118·3 | 1·2805 | 24·895 | 1·1059 | 10·750 |
| 1·39 | 32·4 | 115·5 | 1·2648 | 23·764 | 1·0938 | 9·619 |
| 1·36 | 29·4 | 112·2 | 1·2493 | 22·632 | 1·0819 | 8·487 |
| 1·33 | 26·3 | 109·4 | 1·2342 | 21·500 | 1·0703 | 7·355 |
| 1·28 | 23 4 | 106·6 | 1·2268 | 20·935 | 1·0589 | 6·224 |
| 1·23 | 19·5 | 104·4 | 1·2122 | 19·803 | 1·0478 | 5·002 |
| 1·19 | 16·2 | 103·3 | 1·1979 | 18·671 | 1·0369 | 3·961 |
| 1·15 | 13·0 | 101·7 | 1·1839 | 17·540 | 1·0260 | 2·829 |
| 1·1 | 9·5 | 101·1 | 1·1702 | 16·408 | 1·0153 | 1·697 |
| 1·0 | 4·7 | 100·5 | 1·1568 | 15·277 | 1·0050 | 0·5658 |

The *Liquor Potassæ* of the pharmacopœia contains nearly 5 per cent. of the solid hydrate, KHO, and has a density of 1·058. The strong solution, of specific gravity about 1·25, used for absorbing carbonic acid in organic analysis, may be prepared by dissolving 1 pt. of the hydrate in 3 pts. of water.

*Reactions.*—Hydrate of potassium, when heated alone, does not decompose at any temperature, but when heated with silicic, boric, phosphoric, tungstic, tartaric, stannic, or any non-volatile acid oxide, it gives off water and is converted into a potassium-salt of the acid. Heated with potassium, it gives off hydrogen and is converted into the anhydrous oxide: $KHO + K = K^2O + H$. When moderately heated with sodium under a liquid not containing oxygen, it yields an alloy of potassium and sodium (p. 696). In contact with iron at a white heat, it is completely decomposed, giving off hydrogen and potassium and forming oxide of iron.

Potash possesses in an eminent degree the characteristic properties of an alkali (i. 117), viz., solubility in water; the power of neutralising acids and decomposing metallic salts; a caustic or corrosive action on organic substances; and a peculiar action on vegetable colours, turning reddened litmus blue, turmeric brown, and syrup of violets or infusion of red cabbage, green. Aqueous potash decomposes most metallic salts, precipitating from their solutions all those metals which form insoluble oxides or hydrates. The precipitates formed by it in solutions of aluminium, glucinum, chromium, zinc and lead, are soluble in excess of the alkali; the rest are insoluble. [For the special reactions, see the several metals.]

At high temperatures, it acts with great energy on nearly all substances, taking up any acid that may exist ready formed in the substance, and giving rise, by oxidation, or by a splitting up of the original compound, to the formation of acids which did not previously exist. Thus it decomposes many silicates, forming silicate of potassium and separating the bases: hence it destroys glass or porcelain vessels in which it is fused. Many metals are oxidised by fusion with it, and oxides are raised to a higher state of oxidation; in this manner antimony and arsenic, and even iron and platinum (p. 665), are converted into acid oxides which unite with the potash; and chromic oxide, the oxides of manganese, &c., are converted into chromate and manganate, &c., of potassium.

Organic compounds (carbon-compounds) either unite directly with potash or are decomposed by it, in some cases by contact with its aqueous or alcoholic solution at ordinary or at higher temperatures, in others by fusion with the hydrate. The modes of action of potash (and of fixed alkalis in general) on organic compounds may be classified as follows:—1. Direct combination.—2. Double decomposition.—3. Oxidation with elimination of hydrogen.—4. Conversion of the organic compound into an isomer.

1. The instances of *direct combination* of potash with organic bodies are but few. Carbonic oxide and carbonic anhydride are absorbed by it, producing in the first case, formate of potassium, $CHKO^2$, and in the second, the acid carbonate, $CHKO^3$. Isatin dissolves in aqueous potash, forming isatate of potassium, $C^8H^5NO^2 + KHO = C^8H^6KNO^3$; similarly with chlor- and brom-isatin. Benzil, $C^{14}H^{10}O^2$ and coumarin, $C^9H^6O^2$, are converted by boiling with aqueous potash into benzilate and coumarate of potassium, $C^{14}H^{11}KO^3$ and $C^9H^7KO^3$ respectively; and camphor, $C^{10}H^{16}O$, strongly heated with potash-lime in a sealed tube, is converted into campholate of potassium, $C^{10}H^{17}KO^2$. The acids corresponding to these potassium-salts consist of the original compound $+ H^2O$.

2. *Double Decomposition.*—Organic acids (and indeed all acids) are converted by aqueous potash into potassium-salts with elimination of water: *e.g.*, $C^2H^4O^2 + KHO = C^2H^3KO^2 + H^2O$. Some alcohols (as phenol) yield similar compounds with aqueous potash; solid potash acts also on other alcohols and on aldehydes, but in a different manner.

Some acids when fused with potash at about 200° are resolved into two others, thus:

$$\begin{array}{ccccccccc} C^4H^6O^6 & + & 2KHO & = & C^2H^3KO^2 & + & C^2HKO^4 & + & 2H^2O. \\ \text{Tartaric acid.} & & & & \text{Acetate.} & & \text{Acid oxalate.} & & \\ C^6H^{10}O^8 & + & 3KHO & = & 2C^2H^3KO^2 & + & C^2HKO^4 & + & 3H^2O. \\ \text{Mucic acid.} & & & & \text{Acetate.} & & \text{Acid oxalate.} & & \end{array}$$

Compound ethers are converted by alcoholic potash into alcohols and potassium-salts of the corresponding acids, and glycerides boiled with aqueous potash are resolved into glycerin and potassium-salts of the fat acids, or soaps.

Chlorides, bromides, and iodides of alcoholic and acid radicles are converted by potash into chloride, bromide and iodide of potassium on the one hand, and alcohols or potassium-salts of the acids on the other: *e.g.*:

$$C^2H^5Cl + KHO = KCl + (C^2H^5)HO$$
Chloride of ethyl. — Ethylic alcohol.

$$C^7H^5OCl + 2KHO = KCl + C^7H^5KO^2 + H^2O.$$
Chloride of benzoyl. — Benzoate of potassium.

The chlorides and bromides of diatomic alcohol-radicles (ethylene, amylene, &c.) are resolved under the influence of alcoholic potash into hydrochloric acid and aldehydic chlorides; *e.g.*:

$$C^2H^4Cl^2 = HCl + C^2H^3Cl.$$

Amides (nitrides of acid-radicles) are for the most part attacked by boiling potash, giving off ammonia and yielding potassium-salts of the corresponding acids; *e.g.*:

$$C^7H^5O.H^2.N + KHO = H^3N + C^7H^5KO^2.$$
Benzamide. — Benzoate of potassium.

Alcoholic cyanides boiled with potash give off ammonia and are converted into potassium-salts of fatty acids; *e.g.*:

$$C^2H^5.CN + KHO + H^2O = NH^3 + C^3H^5KO^2.$$

3. *Oxidation with evolution of hydrogen.* This reaction takes place especially with alcohols and aldehydes; thus:

$$C^7H^6O + KHO = C^7H^5KO^2 + H^2.$$
Benzoic hydride. — Benzoate of potassium.

$$C^{10}H^{12}O + KHO = C^{10}H^{11}KO^2 + H^2.$$
Cuminol. — Cuminate of potassium.

$$C^5H^{12}O + KHO = C^5H^9KO^2 + 2H^2.$$
Amylic alcohol. — Valerate of potassium.

Common alcohol and aldehyde are in like manner converted into acetic acid when dropped upon potash-lime.

When the salts produced in these reactions are heated to a temperature higher than that at which they are formed, secondary products are obtained; thus acetate of potassium may be resolved into carbonate and marsh-gas: $C^2H^3KO^2 + KHO = CK^2O^3 + CH^4$; formate of potassium into oxalate and hydrogen: $2CHKO^2 = C^2K^2O^4 + H^2$; the oxalate into carbonate and hydrogen: $C^2K^2O^4 + 2KHO = 2CK^2O^3 + H^2$, &c.

Compound ethers also yield oxidised products when they are fused with potash-lime instead of being treated with alcoholic potash (Dumas and Stas, Ann. Ch. Phys. lxxiii. 151). They then give off hydrogen and yield two kinds of products, the first derived from the acid, the second from the alcohol, as if the alkali had oxidised the acid and alcohol separately. In this manner, ethylic oxalate yields acetic acid derived from the alcohol, and carbonic acid from the oxalic acid.

Like most oxidising agents, potash often splits up organic bodies, especially at very high temperatures, taking from them the carbon and oxygen necessary to convert it into carbonate. Highly oxidised bodies, such as fixed acids, and fixed neutral substances (sugar, gum, starch, woody fibre, &c.) are easily attacked by fused potash, often yielding carbonate and oxalate of potassium, and giving off hydrogen gas. Some acids are resolved by this mode of oxidation into two other acids: thus succinic acid yields oxalic and acetic acids:

$$C^4H^6O^4 + 2KHO = C^2H^3KO^2 + C^2HKO^4 + 3H^2.$$
Succinic acid. — Acetate. — Acid oxalate.

The acids of the acrylic or oleic series fused with potash yield acetic acid and another fatty acid; *e.g.*:

$$C^{18}H^{34}O^2 + 2KHO = C^2H^3KO^2 + C^{16}H^{31}KO^2 + H^2.$$
Oleic acid. — Acetate. — Palmitate.

Azotised bodies (indigo, caffeine, quinine, &c.) subjected to this mode of oxidation with alkaline hydrates give off ammonia or other volatile alkalis; such as methylamine, aniline, chinoline, &c. All nitrogenous organic bodies heated to low redness with hydrate of potassium, yield cyanide of potassium; but when heated to full redness with potash-lime (or soda-lime) they all, excepting nitro-compounds, give off the whole of their nitrogen in the form of ammonia. (See ANALYSIS, ORGANIC, i. 244.)

Organic bodies containing sulphur, yield by fusion with potash, either sulphide, sulphite or sulphate of potassium.

4. A few organic bodies undergo *isomeric or polymeric transformations* by contact with caustic potash; thus furfuramide is converted into furfurine; hydrobenzamide into amarine; bitter almond oil, $C^7H^6O$, into benzoin, $C^{14}H^{12}O^2$.

**POTASSIUM, HYDRIDE OF?** Potassium heated not quite to redness in pure hydrogen gas, absorbs about one-fourth as much of the gas as it would have evolved by contact with water, and is converted into a grey powder, $?HK^4$, without metallic lustre and infusible below a red heat (Gay-Lussac and Thénard). See *Gmelin's Handbook*, iii. 17.

**POTASSIUM, IODIDE OF.** KI.—Potassium unites with solid iodine (under slight pressure, even at ordinary temperatures) and takes fire spontaneously in its vapour, burning with a violet flame. The iodide may be prepared by neutralising hydriodic acid with potash or potassic carbonate; by the action of iodine on aqueous potash or sulphide of potassium; or by decomposing other metallic iodides, those of zinc and iron for example, with carbonate of potassium.

*a.* When iodine is added to a solution of caustic potash till the liquid begins to assume a brown tint, iodide and iodate of potassium are formed, according to the equation:

$$3I^2 + 6KHO = 5KI + KIO^3 + 3H^2O.$$

On evaporating the solution and gently igniting the residue, the iodate is decomposed into iodide and oxygen, and the remaining iodide fuses. Care must be taken not to allow the temperature to rise too high, as the iodide volatilises at a red heat.

*β.* A solution of ferrous iodide is prepared by digesting 2 pts. of iodine and 1 pt. of iron in a stoppered vessel with 10 pts. of water (iii. 390); the solution is decanted after a while from the excess of iron; and a quantity of iodine is added equal to a third of that which it already contains. The solution is then boiled and carbonate of potassium is added by small quantities as long as effervescence ensues and a precipitate is formed. The solution filtered from this precipitate, which consists of ferroso-ferric oxide and is very dense, yields on evaporation, crystals of iodide of potassium. The precipitate however is found to retain a portion of the potassium-iodide with great obstinacy, so that it cannot easily be removed by washing. To obviate this inconvenience Dietz (N. Jahrb. Pharm. xviii. 205) ignites the iron precipitate previously to washing.

*γ.* Liebig (Ann. Ch. Pharm. cxxi. 222) recommends, as the best mode of obtaining pure iodide of potassium, the decomposition of iodide of calcium by sulphate of potassium. To prepare the calcium-iodide, an ounce of amorphous phosphorus is drenched with 30 oz. of hot water, and fine pulverised iodine is gradually added, with constant stirring, as long as it dissolves without colour (the quantity thus dissolved being 13½ oz.). The colourless liquid is then decanted from the slight deposit; the latter is washed; the united clear liquids are mixed to alkaline reaction, with milk of lime prepared from 8 oz. of lime; the solution is strained off; and the residue, consisting of phosphate, phosphite, and excess of hydrate of calcium, is washed. The solution of calcium-iodide thus obtained is mixed with a hot solution of 9 oz. crystallised potassium-sulphate in about 48 oz. water; the liquid, after standing for six hours, is strained from the separated sulphate of calcium; the residue is washed and pressed; the liquid evaporated down to a litre and mixed with carbonate of potassium to precipitate the remaining portion of calcium; and the solution, after the gelatinous precipitate has become dense, is filtered, washed, and evaporated to the crystallising point. This process yields 13½ oz. of crystallised potassium-iodide, and by evaporation of the mother-liquor, 3½ oz. of perfectly pure pulverulent iodide. According to W. Squire (Jahresb. 1862, p. 71), iodide of potassium thus prepared often has a reddish colour [from presence of phosphorus?] and is difficult to crystallise; but may be rendered colourless and easily crystallisable by previous fusion. [For other modes of preparation, see *Gmelin's Handbook*, iii. 45.]

Iodide of potassium, when pure, dissolves in six times its weight of alcohol (specific gravity 0·83), and does not effervesce or turn brown on addition of hydrochloric acid; effervescence would indicate the presence of carbonate, and the production of a brown colour, that of iodate of potassium, the brown colour arising from separation of iodine by the mutual action of iodic and hydriodic acids (iii. 300).

Iodide of potassium crystallises in cubes, sometimes elongated; rarely in octahedrons. The crystals are sometimes transparent, sometimes semi-opaque. Specific gravity = 2·9084 (Karsten); 3·001 (Boullay); 2·850 (Schiff); 3·079 (Schröder). It is not deliquescent, has a sharp taste, and turns reddened litmus-paper slightly blue. It melts below a red heat, and when exposed to the air, volatilises undecomposed at a moderate red heat.

Iodide of potassium is very soluble in water, and in dissolving produces a considerable fall of temperature, sometimes amounting to 24°. It dissolves in 0·735 pt. water at 12·5° and in 0·709 pt. at 16° (Banp); in 0·7 pt. at 18° and in about 0·45 pt. at 120° (Gay-Lussac). A saturated solution boils at 120° (Banp). The following table exhibits the expansion by heat of aqueous solutions of potassium-iodide of various degrees of concentration, as determined by Kremers (Pogg. Ann. cviii. 115; Jahresb. 1859, p. 49):

*Volumes of Aqueous Iodide of Potassium at different temperatures* (vol. at 19·5° = 1).

| Quantity of salt in 100 pts. water. | 28·2 | 56·1 | 92·6 | 135·8 |
|---|---|---|---|---|
| Specific gravity at 19·5°. | 1·1856 | 1·3445 | 1·5144 | 1·6822 |
| 0° | 0·99422 | 0·99231 | 0·99127 | ? |
| 19·5 | 1·00000 | 1·00000 | 1·00000 | 1·00000 |
| 40 | 1·00843 | 1·00959 | 1·01016 | 1·01022 |
| 60 | 1·01856 | 1·02017 | 1·02090 | 1·02085 |
| 80 | 1·03039 | 1·03195 | 1·03247 | 1·03022 |
| 100 | 1·04388 | 1·04500 | 1·04487 | 1·04378 |

Iodide of potassium dissolves at 12·5° in 5·5 pts. *alcohol* of specific gravity 0·85, and at 13·5° in 39—40 pts. of absolute alcohol; hot alcohol dissolves a much larger amount, and deposits it in needles on cooling.

*Chlorine*, with the aid of heat, decomposes iodide of potassium into chloride of potassium and iodine. From a solution in 2 pts. of water, chlorine gas throws down iodine at first; but this disappears again when more chlorine is added, a compound of trichloride of iodine with chloride of potassium being formed, which colours the liquid yellow, and yields an abundant crop of crystals. (Filhol.)

The brownish-yellow colour produced by chlorine is visible in a diluted solution to the extent of 1 pt. of iodide of potassium in 3000 pts. of water; the same reaction is produced by sulphuric and nitric acid, in a solution of 1 pt. in 6000 pts. of water. (See IODIDES, iii. 287.)

Iodide of potassium evaporated with *nitric acid*, is entirely converted into nitrate (Serullas). When it is heated with nitrate of ammonium, iodine is abundantly evolved, with production of a brown colour. It is easily decomposed by *nitrous acid*, which sets the iodine free. On adding nitrite of potassium to a solution of the iodide acidulated with hydrochloric acid and mixed with starch-paste, a dark-blue colour is produced, instantly in strong solutions. after a few seconds in very dilute solutions (D. S. Price, Chem. Soc. Qu. J. iv. 155).—By fusion with *chlorate of potassium*, the iodide is converted into iodate; heated with nitrate of potassium or nitrate of barium, it yields a small quantity of iodate of potassium or barium, together with peroxide of barium in somewhat larger quantity (O. Henry, J. Pharm. xviii. 345). In the vapour of *sulphuric anhydride*, it turns reddish-brown, and produces sulphate of potassium, sulphurous anhydride and iodine (H. Rose, Pogg. xxxviii. 121):

$$2KI + 2SO^3 = K^2SO^4 + SO^2 + I^2.$$

When distilled with dilute sulphuric acid, it yields, first hydriodic acid, then, on further concentration, iodine which dissolves in the hydriodic acid, and sulphurous anhydride which passes over with the water and iodine, and is converted into sulphuric acid. Heated with *peroxide of manganese* and *sulphuric acid*, it gives iodine only, no sulphurous acid. A mixture of equal parts of iodide of potassium, common salt, nitre, and sulphuric acid, yields chloride of iodine as the principal product (Soubeiran). *Steam* passed over iodide of potassium heated to redness, causes the evolution of a large quantity of hydriodic acid gas; the residue is alkaline (Schiodler, Mag. Pharm. xxxi. 33). A mixture of iodide of potassium and *sal-ammoniac* yields, when heated, free iodine, and iodide of ammonium, whilst iodide and chloride of potassium remain behind. The mixture remains unaltered in dry air, but in moist air, slowly absorbs water and becomes brown through the decomposition of the iodide of ammonium.

A concentrated solution of *ferricyanide of potassium* separates iodine from iodide of potassium; a dilute solution does not; and the iodine separated in the former case is taken up again on diluting the liquid, the reaction represented by the equation $2K^3Fe'''Cy^6 + 2KI = 2K^4Fe''Cy^6 + I^2$, taking place one way or the other according to the strength of the solutions. (C. Mohr, Ann. Ch. Pharm. cv. 57; Jahresb. 1858, p. 99.)

Iodide of potassium is much used in medicine; it is not poisonous even in doses of several drachms. Its solution is also employed as a vehicle for iodine itself, 20 grs. of iodine and 30 grs. of the iodide being usually dissolved together in an ounce of water. The solution thus obtained, which has a dark-brown colour, is sometimes supposed to contain a di-iodide of potassium; but as the excess of iodine is easily removed from it by sulphide of carbon, this view is not very probable.

Iodide of potassium unites with many other metallic iodides, forming double salts; these are described under the respective metals. A compound of iodide and ferricyanide of potassium, $KI.K^3Fe'''Cy^6$, is obtained as a golden-yellow crystalline powder by the action of iodine on a warm solution of the ferrocyanide. (Preuss, Ann. Ch. Pharm. xxix. 323.)

**POTASSIUM, NITRIDE OF.** Tripotassamide, $K^3N$ (p. 695).

**POTASSIUM, OXIDES OF.** Potassium forms three oxides, a protoxide $K^2O$, a dioxide $K^2O^2$, and a tetroxide $K^2O^4$. A grey suboxide is said also to be formed during the gradual oxidation of the metal in dry air, but it is probably only a mixture of the protoxide with potassium.

*Protoxide of Potassium* or *Anhydrous Potash*, $K^2O$, is formed: 1. When potassium in thin slices is exposed at ordinary temperatures to air free from moisture and carbonic anhydride.—2. By heating potassium with various metallic oxides, also with carbonic, boric, silicic, sulphuric anhydride, &c.—3. By heating 1 at. potassium with 1 at. of the hydrate:—

$$2KHO + K^2 = 2K^2O + H^2.$$

Protoxide of potassium is white, very deliquescent and caustic; combines energetically with water, becoming incandescent when moistened with it; melts at a red heat and volatilises at very high temperatures.

*Tetroxide* or *Peroxide of Potassium*, $K^2O^4$.—This oxide is obtained, mixed however with variable quantities of the protoxide, when potassium is burnt in dry air or oxygen gas. Gay-Lussac and Thénard, who examined the peroxide thus formed, assigned to it the composition $K^2O^3$, but their determinations did not agree well with one another. To obtain a definite product, it is necessary to expose perfectly pure and clean potassium to a moderate heat, first in a current of dry air, then in dry oxygen gas; if the metal is at once exposed to the action of pure oxygen, great heat is evolved, and the peroxide melts and attacks the glass vessel.

Tetroxide of potassium is a chrome-yellow powder which cakes together at about 280°. It absorbs moisture rapidly from the air, and is decomposed by *water*, giving off 2 at. oxygen, and forming a solution of dioxide of potassium, $K^2O^2$. When heated in a *silver* boat in an atmosphere of nitrogen, it is reduced to protoxide, oxide of silver being also formed and 2 at. oxygen given off as gas:—

$$K^2O^4 + Ag^2 = K^2O + Ag^2O + O^2.$$

When heated with *sulphur*, it deflagrates violently; but when sulphur-vapour is passed over the tetroxide gently heated in an atmosphere of nitrogen, a portion of it (in one experiment nearly the whole) is converted into sulphate of potassium $KO^4S$; generally however the excess of sulphur exerts a reducing action, forming sulphurous anhydride and sulphide of potassium. The tetroxide gently heated in a stream of *carbonic oxide*, yields carbonate of potassium and 2 at. oxygen, $K^2O^4 + CO = CK^2O^3 + O^2$. With *carbonic anhydride*, a similar action takes place, with evolution of 3 at. oxygen. With *nitric oxide*, it forms nitrate and nitrite of potassium, together with nitric peroxide:

$$K^2O^4 + 3NO = KNO^3 + KNO^2 + NO^2.$$

Nitrous oxide does not act upon it. (A. Vernon Harcourt, Chem. Soc. Qu. J. xiv. 267.)

*Dioxide of Potassium*, $K^2O^2$, is formed at a certain stage in the preparation of the tetroxide, but has not been obtained in perfectly definite form. By carefully regulating the heat and the supply of air, nearly the whole of the potassium may be converted into a white oxide exhibiting nearly the composition of the dioxide; but before the metal has quite disappeared, some portions of it are always converted into the yellow tetroxide. An aqueous solution of the dioxide is formed, as already observed, by the action of water on the tetroxide. (Harcourt.)

**POTASSIUM, PHOSPHIDE OF.**—Potassium and phosphorus unite when heated together in nitrogen gas, the combination being attended with evolution of light and heat. Under naphtha the action takes place without combustion, merely causing the liquid to boil. To obtain the pure phosphide, potassium must be heated with excess of phosphorus in a stream of hydrogen till flame is produced, and further till the mass of phosphorus is volatilised (H. Rose, Pogg. Ann. xii. 547). It is a copper-red, crystalline substance having a metallic lustre. It burns rapidly when heated in the air, forming phosphate of potassium, and is decomposed by water, yielding hypophosphite of potassium, phosphoretted hydrogen gas, and solid phosphide of hydrogen. (H. Rose.)

**POTASSIUM, SELENIDES OF.**—Compounds of selenium and potassium in various proportions are obtained: 1. By direct combination. 2. By igniting selenite or selenate of potassium with hydrogen or charcoal. 3. By fusing selenium with hydrate or carbonate of potassium, selenite of potassium being formed at the same time. The products thus formed are grey or brown masses which dissolve in water, forming a solution from which acids eliminate gaseous selenide of hydrogen, and precipitate selenium if that element is in excess. A solution of selenide of potassium may also be formed by boiling selenium for a long time in aqueous potash. All the solutions of potassium-selenide have a hepatic taste, and on exposure to the air, deposit selenium in the form of a red powder.

**POTASSIUM, SILICIDE OF.**—The two elements, when heated together, unite without perceptible incandescence. The compound containing a larger proportion of potassium than silicium is dark greyish-brown, and dissolves entirely in water, with evolution of hydrogen gas, yielding silicate of potassium; the compound with more silicium than potassium—obtained by decomposing fluoride of silicium with potassium, and also by strongly igniting the first compound—leaves a residue of silicium when digested in water. When vapour of potassium is passed over ignited silica, silicate and silicide of potassium are produced, and dissolve in water without leaving any residue. But if the greater part of the potassium be previously expelled at a strong red heat, and the remaining vitreous mass digested in water and then in hydrofluoric acid, a small quantity of silicium is left behind.

**POTASSIUM, SILICOFLUORIDE OF.** $K^2SiF^6 = 2KF.SiF^4$.—Obtained by adding hydrofluosilicic acid to a potassium-salt, as a transparent gelatinous precipitate, which dries up to a white earthy powder. It is one of the least soluble of the salts of potassium; consequently hydrofluosilicic acid is sometimes used to separate potassium from its solutions, as in the preparation of chloric acid from chlorate of potassium.

**POTASSIUM, SULPHIDES OF.** Potassium heated in sulphur-vapour readily takes fire and burns with great brilliancy. It unites with sulphur in five different proportions, viz. $K^2S$, $K^2S^2$, $K^2S^3$, $K^2S^4$, and $K^2S^5$.

*Protosulphide*, $K^2S$.—It is doubtful whether this compound has been obtained in the pure state. It is commonly said to be produced by heating sulphate of potassium in a current of dry hydrogen, or by igniting the same salt in a covered vessel with finely divided charcoal; but according to Bauer (J. pr. Chem. lxxv. 246; Jahresb. 1858, p. 116), one of the higher sulphides is always formed at the same time, together with oxide of potassium. The product has a reddish-yellow colour, is deliquescent, and acts as a caustic on the skin. When sulphate of potassium is heated in a covered crucible with excess of lamp-black, a mixture of sulphide of potassium and finely divided carbon is obtained, which takes fire spontaneously on coming in contact with the air. The protosulphide might perhaps be obtained pure by heating 1 at. sulphydrate of potassium, KHS, with 1 at. of the metal.

When sulphydric acid gas is passed to saturation into a solution of caustic potash, a solution of the sulphydrate is obtained, which is colourless at first, but if exposed to the air, quickly absorbs oxygen, and turns yellow in consequence of the formation of disulphide: $2KHS + O^4 = K^2S^2 + H^2O$. If a solution of potash be divided into two equal parts, and one half be saturated with sulphydric acid, and then mixed with the other, a solution is formed which may contain protosulphide of potassium: $KHS + KHO = K^2S + H^2O$; but it is also possible that the hydrate and the sulphydrate may mix without mutual decomposition. The solution when mixed with one of the stronger acids, gives off sulphydric acid without deposition of sulphur, a reaction which is consistent with either view of its consititution.

*Disulphide of Potassium*, $K^2S^2$, is formed, as already observed, on exposing a solution of the sulphydrate to the air till it begins to show turbidity. By evaporation in a vacuum, it is obtained as an orange-coloured, easily fusible substance.

The *trisulphide*, $K^2S^3$, is obtained by passing the vapour of carbonic disulphide over ignited carbonate of potassium as long as gas continues to escape:

$$2K^2CO^3 + 3CS^2 = 2K^2S^3 + 4CO + CO^2;$$

also, together with sulphate of potassium—forming one of the mixtures called *liver of sulphur*—by melting 69 pts. (4 at.) carbonate of potassium with 40 pts. (10 at.) sulphur (p. 708):

$$4K^2CO^3 + S^{10} = K^2SO^4 + 3K^2S^3 + 4CO^2.$$

The *tetrasulphide*, $K^2S^4$, is formed by reducing sulphate of potassium with the vapour of carbonic disulphide.

The *pentasulphide*, $K^2S^5$, is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till it is saturated, or by fusing either of them in the dry state with sulphur. The excess of sulphur then separates and floats above the dark liver-brown pentasulphide.

All the sulphides of potassium are brown or yellow-brown solids, having an alkaline reaction to test paper, and smelling more or less distinctly of sulphydric acid. Acids decompose them, with evolution of sulphydric acid gas, attended, in the case of all but the protosulphide, with the precipitation of white, finely divided sulphur (milk of sulphur). On adding the pentasulphide to an excess of hydrochloric acid of specific gravity about 1·1, persulphide of hydrogen, $H^2S^2$ (iii. 204), is separated as an oily liquid. The solutions of the higher sulphides become colourless on exposure to the air, the sulphide being oxidised to hyposulphite and the excess of sulphur separated. When a solution of caustic potash is boiled with sulphur, a decomposition ensues similar to that which occurs when hydrate of potassium and sulphur are fused together; a deep reddish liquid is then formed containing hyposulphite of potassium and one of the higher sulphides: *e.g.*

$$6KHO + S^{12} = K^2S^2H^2O^4 + 2K^2S^5 + 2H^2O.$$

*Liver of Sulphur, Hepar sulphuris salinum s. alcalinum*, which is prepared by gently heating sulphur with carbonate of potassium in closed vessels, *e.g.* in covered earthen or cast-iron crucibles,—but freest from impurity, in glass flasks,—consists of trisulphide, penta-sulphide and intermediate sulphides of potassium, according to the proportions employed, mixed with sulphate and often at the same time with carbonate of potassium. 69 pts. (4 at.) carbonate of potassium and 40 pts. (10 at.) sulphur yield a mixture of 1 at. sulphate and 3 at. sulphide of potassium (p. 707). When less sulphur is used and a lower heat applied, the product likewise contains undecomposed carbonate of potassium; if the heat be stronger, the trisulphide changes to the disulphide, and a larger quantity of potassic carbonate is decomposed. Lastly, if the amount of sulphur exceeds 10 at., the excess converts the disulphide into tetra- or penta-sulphide of potassium. 4 at. carbonate of potassium require 16 at. of sulphur to form pentasulphide. Consequently, for 69 pts. carbonate of potassium, 40 pts. of sulphur is the smallest quantity that can be used, and this produces tri-sulphide of potassium; 64 pts. is the largest, penta-sulphide being produced; any excess of sulphur beyond this volatilises without entering into combination. In the common proportion of 2 pts. of carbonate of potassium to 1 pt. of sulphur, the quantity of sulphur is therefore too small.

**POTASSIUM, SULPHOCARBONATE OF.** See SULPHOCARBONATES.

**POTASSIUM, SULPHOCYANATE OF.** See SULPHOCYANATES.

**POTASSIUM, SULPHOMOLYBDATE OF.** See MOLYBDENUM, SULPHIDES OF (iii. 1044.)

**POTASSIUM, SULPHOPHOSPHATE** and **SULPHOPHOSPHITE OF.** See PHOSPHORUS, SULPHIDES OF (pp. 603, 604).

**POTASSIUM, SULPHOTUNGSTATE** and **SULPHOVANADATE OF.** See TUNGSTEN and VANADIUM, SULPHIDES OF.

**POTASSIUM, SULPHYDRATE OF.** $KHS$ or $K^2S.H^2S$.—Formed, with liberation of 1 at. hydrogen, when 1 at. potassium is heated in 1 at. sulphydric acid gas, *e.g.* when 200 c. c. of the gas are decomposed by a quantity of potassium capable of evolving 100 c. c. of hydrogen from water: $2H^2S + K^2 = 2KHS + H^2$ (Gay-Lussac and Thénard); also by passing sulphydric acid gas over carbonate of potassium at a low red heat as long as water and carbonic anhydride continue to pass off (Berzelius):

$$K^2CO^3 + 2H^2S = 2KHS + CO^2 + H^2O.$$

It is white if air has been excluded during its preparation, yellowish in the contrary case; crystalline; black when melted. It is decomposed by dilute acids, with evolution of sulphydric acid If heated with 1 at. potassium, it would probably yield the pure protosulphide: $2KHS + K^2 = 2K^2S + H^2$. The same compound is obtained in solution by saturating aqueous potash with sulphydric acid (p. 707).

**POTASSIUM, TELLURIDE OF.** Formed by heating tellurium with potassium in an atmosphere of hydrogen; by heating telluric oxide with 2 pts. hydrate of potassium and 1 pt. charcoal; and by passing the current of a powerful voltaic battery through a solution of potash with tellurium for the negative pole. The compound obtained by the first method is dark copper-coloured, brittle, has a crystalline fracture, and does not melt below a red heat; that obtained by the second has the colour of nickel, while the third yields a steel-grey, brittle compound much more fusible than pure tellurium. Telluride of potassium dissolves in water, forming a purple solution which becomes colourless and deposits tellurium on exposure to the air, and gives off telluride of hydrogen when treated with acids. A similar solution, but containing also tellurite of potassium, is formed by boiling tellurium in aqueous potash. (Berzelius.)

**POTASSIUM-ETHYL,** $C^2H^5K$, and **POTASSIUM-METHYL,** $CH^3K$, are obtained in combination with zinc ethyl and zinc-methyl, by treating those compounds with potassium; they are not known in the separate state. Their reactions are precisely analogous to those of the corresponding sodium-compounds (*q. v.*).

**POTASSIUM-SALTS, MANUFACTURE OF.** The sources of potassium have been already enumerated. Formerly nearly all the potash used in the arts and manufactures was obtained from the ashes of land-plants; but of late years the increasing demand for potash for the preparation of various compounds in which it has not yet been found possible to replace that alkali by soda, namely the chlorates, prussiates, chromates, &c., and more especially of saltpetre for the manufacture of gunpowder—also as a manure for the cultivation of various plants (vine, beet, cereals, &c.)—has led to the invention of several processes by which potassium salts may be obtained, either directly from mineral sources, or from the waste products of manufacturing operations. It must be observed, however, that the incineration of land plants has the advantage of yielding the alkali in the form of carbonate, which may easily be converted into the other salts by neutralisation with the respective acids, or into caustic potash by boiling with lime (p. 700), and thus at once rendered available for the manufacture of soap, and the various other purposes for which a caustic alkali is required, whereas the other sources yield the potassium for the most part in the form of chloride or sulphate, that is to say in a form resembling the crude material in Le Blanc's process for the preparation of soda, and requiring a complicated series of operations to convert it into carbonate or caustic alkali. For some purposes however, the preparation of nitrate of potassium for example, the chloride of potassium is at once available, without previous conversion into carbonate.

The sources from which potassium-salts are at present obtained are the following:

| | |
|---|---|
| I. The ashes of Land plants. | IV. Felspar and other Silicates. |
| II. The ashes of Marine plants. | V. The Wool of Sheep. |
| III. Sea-water, Brine-springs, and Saline deposits. | |

### I. MANUFACTURE OF CARBONATE OF POTASSIUM FROM THE ASHES OF TIMBER AND OF LAND PLANTS IN GENERAL.

The ashes obtained from plants of different species exhibit very great diversities of quantity and composition; but the chief constituents are always the carbonates, chlorides, sulphates, phosphates, and silicates of potassium, sodium, calcium, magnesium, and iron: the carbonates, which generally constitute by far the larger proportion of the ash, are produced by the decomposition of organic salts of the several bases (see ASH OF ORGANIC BODIES, i. 416). The following tables will give an idea of the great differences in the total amount of ash and the proportion of potash yielded by various plants:

Höss: *Analyses from* 1,000 *parts.*

| | Ash. | Potash ($K^2O$). |
|---|---|---|
| Pine wood | 3·40 | 0·45 |
| Beech " | 5·80 | 1·27 |
| Ash " | 12·20 | 0·74 |
| Oak " | 13·50 | 1·50 |
| Elm " | 25·50 | 3·90 |
| Willow " | 28·00 | 2·85 |
| Vines | 34·00 | 5·50 |
| Ferns | 36·40 | 4·25 |
| Wormwood | 97·40 | 73·00 |
| Fumitory | 219·00 | 79·90 |

Abbene and Blengini: *Analyses from* 1,000 *parts.*

| | Ash. | Potash ($K^2O$). |
|---|---|---|
| Dahlia with blossoms and leaves | 79·92 | 19·98 |
| " stems after flowering time | 44·57 | 3·60 |
| " bulbs | 99·16 | 13·44 |
| " branches | 23·05 | 2·56 |
| Acacia-branches | 24·59 | 2·56 |
| Grape-stems | 88·88 | 41·66 |
| Vine | 46·66 | 12·73 |
| Skins of pressed grapes | 72·91 | 14·88 |
| Stems of a cluster of grapes | . . | 39·81 |
| Grape-stones | . . | 9·50 |

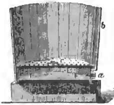
More extensive tables will be found in Richardson and Watts's *Chemical Technology*, i. [3] 440—453.

### 1. *Potash from the ash of Forest-timber.*

It will be seen from the examples above given that the proportion of potash in herbaceous plants is much greater than in trees; and accordingly it has been proposed to grow such plants (wormwood, tansy, marigold, &c.) for the sole purpose of extracting potash from their ashes. But such a plan can seldom be profitably carried out: for these fast-growing plants, except under very peculiar circumstances, soon exhaust the soil of all its available potash. Forest trees, on the other hand, during their comparatively slow growth, are able to avail themselves of the potash which is supplied to the soil by the gradual decomposition of felspar, clay, &c., and thus a continuous growth is kept up without exhaustion of the soil. It is therefore from forest trees that potash is principally obtained, the manufacture being carried on in countries where extensive forests prevail, as in North America, Russia, Sweden, Germany, and some parts of Tuscany and France.

The incineration is effected either in pits, sunk into the ground to a depth of three or four feet, or the plants and timber are arranged in piles on the ground, fresh quantities of timber being added, in either case, until a heap of ashes is obtained.

Fig. 741.

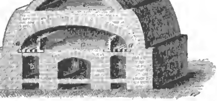


*The lixiviation of the ashes.*—The ash is sifted from the coal and charred wood, thoroughly moistened and filled into two rows of common wooden cisterns or half barrels (*fig.* 741), the two rows being arranged one above the other, with a third row of empty cisterns, or wells, on a still lower level. The cisterns have false (sieve-like) bottoms covered with straw, from which the lye, when sufficiently strong, is drawn into the evaporating pans. The method of lixiviation, generally with cold, sometimes with hot water, is similar to that practised in alkali-works. The upper row of cisterns is first filled with water on the top of the firmly pressed down ash, and drawn when the lixiviation is complete; they are then refilled and the weak lye is run into the first ash-cistern of the second row, whence it also issues in a fit state of saturation for boiling; this system is continued in rotation, every fresh portion of water coming at last in contact with a fresh portion of ash. The lye in its proper state of saturation should contain from 20 to 25 per cent. of salt. This simple and most effectual method is however only one out of a great number, used in different countries, for the description of which see Richardson and Watts's *Chemical Technology*, i. [3] 458.

*Evaporation of the lye.*—The lye, which is of a dark-brown colour, is evaporated in flat iron pans, whilst the water is constantly replaced by lye of the proper strength, until the contents of the pan become thick, and the hot lye quickly solidifies on cooling; the whole is then evaporated to dryness with constant stirring. The crude product thus obtained is called, from the mode of preparation, crude potash or potashes. It consists mainly of carbonate of potassium, with a considerable quantity of sulphate and about 12 per cent. of water.

In Germany the sulphate of potassium is sometimes separated by allowing it to crystallise out of the liquor, before boiling down. In Russia, potashes are made largely from wood-ashes or the ash of straw, as a duty from the peasantry to the estate-owners. The lye is evaporated in flat copper pans to the point of crystallisation, and the carbonate of potassium deposits in brown crystals, which are then calcined in a muffle furnace.

Fig. 742.



*Calcination.*—Crude potash contains water and empyreumatic substances, and these are destroyed by calcination. The calcining furnace is shown in *fig.* 742, and is worked in the same manner as the carbonating furnace in the manufacture of alkali; the crude potash, first covering the hearth in a thin layer, is well paddled and turned, then broken down and thoroughly exposed to the hot air, until all combustible matter is destroyed and the whole mass acquires a clear and bright flame-red heat, when a sample, after cooling, will appear quite white. Careful management is required throughout the operation to prevent the fluxing of the mass and to give the ash a bright appearance. The loss in weight by calcining the crude potash is from 15 to 20 per cent. The calcined product, called pearl-ash, is packed while still hot, to prevent any absorption of moisture. The ash is often discoloured by impurities. In some manufactories, a muffle furnace is used instead of that above described.

*Refining of Pearl-ash.*—In America the pearl-ash is sometimes redissolved, the liquor concentrated and the less soluble salts are allowed to crystallise out; the clear liquor is then evaporated to dryness with constant stirring; this ash is called "salt of tartar." In France the calcined pearl-ashes are washed several times with cold water, which gradually takes up all the carbonate of potassium, and the solution (specific gravity about 1·4735) is evaporated in a system of pans. The pearl-ash thus produced is of first-rate quality, and very much liked in commerce on account of its granular form.

*Commercial Potashes.*—There is a great variety of potashes, according to the locality where they are made, whence they are imported, &c.—The American, imported in oak casks viâ New York and Philadelphia, are reddish, sometimes grey and violet, hard, but very deliquescent; there are three kinds, containing respectively 54 to 58 per cent., 48 to 52 per cent. and 30 to 45 per cent. of neutral carbonate of potassium, $K^2CO^3$.—The white American, or pearl-ash, is granular, varying in percentage from 25 to 58 per cent.—The Russian, St. Petersburg or Odessa, also called "Kasan" from being manufactured near this locality, are packed in poplar casks, and contain from 50 to 52 per cent. of pure carbonate.—The Riga potashes are similar, and vary from 50 to 52 per cent.—The Polish (*Potasse de Paille*) are denser and harder.—The Dantzig resemble pearl-ashes, but are more friable, and stand from 50 to 60 per cent.—There are three qualities of the Tuscan, which are in powder, mixed with pieces of different colours: grey of 60 per cent.; white, harder, of 50 to 55 per cent.; and blue of the same strength.—All other potashes are of a similar character; they are never completely soluble in water, and sometimes leave a considerable residue.

The following analyses give a very good idea of the composition of the various kinds of commercial potashes:

I. Hermann's *Analysis of Potashes from Kasan.*

*Insoluble portion.*

| | | |
|---|---|---|
| Lime | 0·054 | |
| Alumina | 0·012 | |
| Manganic acid | 0·013 | |
| Silica | 0·132 | 0·211 |

*Soluble portion.*

| | | |
|---|---|---|
| Carbonic acid | 27·790 | |
| Potash | 47·455 | |
| Soda | 2·730 | |
| Sulphate of potassium | 17·062 | |
| Chloride of potassium | 3·965 | |
| Bromide of potassium | trace | |
| Phosphate of potassium | 0·443 | |
| Silica | 0·344 | 99·789 |
| | | 100·000 |

II. Pesier's *Analyses of Commercial Potashes.*

| Constituents. | Tuscany. | Russia. | America. | | Vosges. |
|---|---|---|---|---|---|
| | | | Red. | Pearl-ashes. | |
| Carbonate of potassium | 74·10 | 69·61 | 68·07 | 71·38 | 38·63 |
| Carbonate of sodium | 3·01 | 3·09 | 5·85 | 2·31 | 4·17 |
| Sulphate of potassium | 13·47 | 14·11 | 15·32 | 14·38 | 38·84 |
| Chloride of potassium | 0·95 | 2·09 | 8·15 | 3·64 | 9·16 |
| Insoluble matters | 0·65 | 1·21 | 3·35 | 0·44 | 2·66 |
| Moisture | 7·28 | 8·82 | not estimated | 4·56 | 5·34 |
| Phosphoric acid, lime, silica, &c. and loss | 0·54 | 1·07 | | 3·29 | 1·20 |
| | 100·00 | 100·00 | | 100·00 | 100·00 |

III. Bley's *Analyses of Illyrian Potashes.*

| | | |
|---|---|---|
| Carbonate of potassium | 78·75 | 82·85 |
| Carbonate of sodium<br>Sulphate of sodium | 12·50 | 12·50 |
| Insoluble matter | 8·75 | 4·65 |
| | 100·00 | 100·00 |

IV. Van Bastelaer's *Analyses of American and Russian Potashes.*

| Constituents. | American potashes. | | | Russian potashes. |
|---|---|---|---|---|
| | 1 | 2 | 3 | |
| Carbonate of potassium | 21·47 | 30·43 | 12·96 | 50·84 |
| Caustic potash | 4·46 | 9·33 | 21·71 | |
| Sulphate of potassium | 20 08 | 25·05 | 23·70 | 17·44 |
| Chloride of potassium | 7·55 | 4·20 | 7·89 | 5·80 |
| Carbonate of sodium. | 22·99 | 23·90 | 17·07 | 12·14 |
| Moisture | 9·37 | 3·11 | 0·81 | 10·18 |
| Insoluble matters | 14·08 | 3·98 | 15·86 | 3 60 |
| | 100·00 | 100·00 | 100·00 | 100 00 |

V. Meyer's *Analyses of American Potashes* (New York).

| Constituents. | Best Quality. | | First Quality. | Second Quality. | | Third Quality. |
|---|---|---|---|---|---|---|
| Carbonate of potassium | 43·68 | 24·57 | 56·01 | 15·07 | 53·15 | 38·47 |
| Hydrate of potassium | 49·68 | 44·43 | 5·61 | 38·69 | 4·49 | |
| Sulphate of potassium | 4·07 | 16 14 | 27·70 | 19·76 | 21·30 | 53·34 |
| Chloride of sodium | 1·64 | 4·40 | 10·49 | 6·60 | 5·37 | 0·62 |
| Carbonate of sodium | . . | 4·27 | . . | 4·70 | 14·01 | 6·03 |
| Insoluble matter | 0·72 | 6·19 | 0·19 | 15·86 | 1·69 | 1·54 |
| | 99·79 | 100·00 | 100·00 | 100·68 | 100·01 | 100·00 |

2. *Potash as a bye-product from the manufacture of Beet-root and Cane-sugar.*

Beet-root is a potash-plant, its ash containing only in some few instances a large proportion of soda; thus Boussingault found in the two kinds:

| | Potash-ash. | Soda ash. |
|---|---|---|
| Potash | 48·9 | 30·1 |
| Soda | 7·6 | 34·2 |
| | = 100 | = 100. |

Mathieu de Dombasle first attempted to combine the production of sugar with the extraction of potash by incinerating the leaves of the beet-root; his plan was however soon abandoned; about 20 years later, Dubrunfaut suggested that the uncrystallisable sugar in the molasses should be converted into alcohol, and the potassium-salts extracted from the residue. This plan, which has been adopted on a large scale in France and Germany, depends on inducing a fermentation in the molasses, separating the alcohol by distillation, evaporating the residual liquors to dryness, calcining the solid mass, and treating the pure salts as described for ordinary potashes.

*Molasses.*—The uncrystallisable sugar in raw beet-root sugar was found by Moinier to vary from 0·12 to 3·40 per cent., but in some molasses it amounts to 90 per cent. Payen, Poinsot, and Brunet found 9·699 per cent. of the carbonates of potassium and sodium in this material. Krocker found in the mineral matter left by the incineration of the molasses:—

| | $K^{2}O$. | $Na^{2}O$. | CaO. | $SO^{3}$. | $SiO^{2}$. | $CO^{2}$. | $P^{2}O^{5}$. | Earthy Phosphate. | NaCl. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Soluble | 47·88 | 2·34 | . . | 1·53 | 0·85 | 22·39 | . . | . . | 12·92 | = | 87·91 |
| Insoluble | 1·70 | 0·17 | 5·29 | . . | 0·22 | 3·79 | 0·29 | 0·63 | . . | = | 12·09 |
| | | | | | | | | | | | 100·00 |

The molasses are diluted to a specific gravity of 1·085, and sulphuric acid is added to render the liquid slightly acid. This liquid is mixed with 2½ per cent. of the yeast of beer, run into large cisterns, exposed to a temperature of 20° C. (68° F.) and allowed to ferment for five or six days. It is then distilled to separate the alcohol, amounting to 4 or 5 per cent. of the liquid. All the salts contained in the plant remain in the residue called vinasse.

This residue is neutralised with chalk, and the liquid is allowed to settle. It is then concentrated in iron pans to a syrupy consistence (1·217 to 1·372 specific gravity), run into tanks to allow the sulphate of calcium to precipitate, and the clear brown liquor is calcined in a reverberatory furnace.

The addition of chalk to the vinasse is most beneficial to the composition of the salt produced, as is plainly shown in the following comparative analyses:—

| | Without lime. | With lime. |
|---|---|---|
| Carbonate of potassium | 42 | 52 |
| Carbonate of sodium | 29 | 30 |
| Sulphate of potassium | 10 | 1 |
| Sulphide of potassium | 3 | |
| Chloride of potassium | 16 | 17 |
| | 100 | 100 |

The potashes obtained in this process vary very much according to the districts where the beet-root has been grown; they are richer where the beet-root has recently been introduced, than where the soil has been long cultivated and is consequently exhausted. These raw beet-root potashes, called "Salin" on the continent, contain on the average:—

| | |
|---|---|
| Sulphate of potassium, from | 3 to 5 per cent. |
| Chloride of potassium, „ | 20 per cent. |
| Carbonate of potassium „ | 30 to 35 per cent. |
| Carbonate of sodium „ | 18 per cent. |

*Refining of the raw Salin.*—The crude material is lixiviated and the liquors are sometimes boiled down to dryness; sometimes the strong liquors are concentrated up to 1·473 whilst the sulphate of potassium is fished out. After cooling, a large crop of crystals of chloride of potassium forms in the coolers. The mother-liquor is separated, concentrated up to specific gravity 1·555, and again run into coolers. In three or four days a mass of crystals is formed, consisting of a double carbonate of potassium and sodium. The mother-liquor, now very rich in carbonate of potassium, is boiled down to dryness. By redissolving and recrystallising, another double salt with less carbonate of potassium is formed, which is then melted in a metal pan and boiled, whereupon carbonate of sodium with 1 at. water ($Na^2CO^3.H^2O$) separates, leaving the mother-liquor rich in potassium-salt.

M. Billet subjects the vinasse to a distillation process, somewhat similar to that which Mr. Stanford has proposed for seaweed, whereby he obtains tar, illuminating gas and charcoal in addition to the ash. The potash is extracted by lixiviation, with less loss than in the previous process, and in a state of much greater purity. (See Richardson and Watts's *Chemical Technology*, i. [3] 480.)

The aggregate quantity of potassium-salts produced from the beet-root manufacture in Europe must be very large, and is daily increasing. The application of these processes to similar waste-products in the manufacture of cane-sugar might be equally advantageous; a process has in fact been patented by Mr. G. Seymour for Mons. Leplay, for the recovery of the potash and soda from the saccharine juices of canes or beet-root by means of caustic baryta.

### 3. *Sulphate and Carbonate of Potassium as bye-products in the manufacture of Tartaric Acid.*

The acid tartrate of potassium existing in grape juice being but slightly soluble in a mixture of alcohol and water, is separated during fermentation as a crust on the sides of the casks, and called white or red crude tartar according to the wine from which it is obtained. This being dissolved in hot water, and the saturated solution allowed to cool, the surface is soon covered with a coating of fine crystals of the acid tartrate which in this state is called cream of tartar. The best kinds come from Italy, Spain, and France, and contain on an average from different samples 82·7 per cent. acid tartrate of potassium, 7·6 tartrate of calcium, and 9·7 water (*Technology*, i. [3] 484).

These tartars when heated are decomposed, and leave a black mass called "black flux;" consisting of potassium-carbonate mixed with charcoal; when they are deflagrated with saltpetre, a white residue is obtained called "white flux;" consisting mainly of potassium-carbonate. Both of these fluxes are extensively used in assaying metallic ores. The tartars were formerly heated in the open air, till the residue became white, and then sold as wood-ash.

The lees of wine, as well as the yeast, are now used for the production of carbonate of potassium. After the fermentation of the wine, the yeast or lees is collected into one vessel, placed in bags, and pressed; and the cakes are dried and incinerated. Great care is required in regulating the fire properly. These ashes, in France called *Cendres gravelées*, are of a very superior quality, very light, porous and white. A similar product is obtained from the residue in the manufacture of brandy.

In the manufacture of tartaric acid half the acid in the crude tartar is neutralised with lime and precipitated as tartrate of calcium. The neutral tartrate of potassium remains in solution, and may be converted into chloride or sulphate of potassium, by means of chloride of calcium, sulphate of calcium, or dilute sulphuric acid. Mr. Gatty has patented a process, by which he obtains the alkali in the form of a carbonate by treating the solution of neutral tartrate with milk of lime, forcing carbonic acid gas at the same time into the liquid until it is saturated; insoluble tartrate of calcium is formed, and the acid carbonate of potassium, which remains in solution, is evaporated and calcined in a reverberatory furnace.

Wagner proposes to substitute carbonate of barium for the lime, and obtains thus insoluble tartrate of barium and a solution of neutral tartrate of potassium, which latter he mixes with a solution of hydrate of barium. This mixture is boiled and carbonic acid passed through it, until all the baryta is precipitated, and the caustic potash is converted into carbonate, which is then evaporated and dried.

### II. From the Ashes of Marine Plants.

The value of marine plants as a source of alkali has been known from a very early age; the systematic production of the ash of seaweed, called "kelp" in this country, "varec" in France, is, however, at least in these islands, of comparatively recent origin. First regularly pursued in Ireland, it was introduced into Scotland by Mr. M'Leod about the year 1730. It was at first worked, for its contents of carbonate of sodium, at the time when high war duties were levied on barilla and salt. At the beginning of the present century, the value of Highland kelp was twenty pounds per ton, and the production of Scotland about this period was 20,000 tons per annum. When the manufacture of soda from common salt commenced, the kelp fell rapidly in value, and, although the discovery of iodine in 1812 opened up a new demand for kelp, its production never again reached the above-named amount. Kelp and varec are now produced solely for their contents of iodine and potassium-salts.

Tables of the composition of the ash of seaweed are given in Richardson and Watts's *Chemical Technology* (i. [3] 501, 502), showing that the

| | | | | | |
|---|---|---|---|---|---|
| Potash and soda vary | from | 15 | to | 40 | per cent. |
| Lime | „ | 3 | „ | 21 | „ |
| Magnesia | „ | 7 | „ | 15 | „ |
| Common salt | „ | 3 | „ | 35 | „ |
| Phosphate of calcium | „ | 3 | „ | 10 | „ |
| Sulphuric acid | „ | 14 | „ | 31 | „ |
| Silica | „ | 1 | „ | 11 | „ |

*Collection of the Seaweed and manufacture of the Kelp.*—In Scotland the kelp is collected from June to September, and is known as "cutweed" and "driftweed." The cutweed or weed cut from the rocks, is chiefly obtained in the Highlands from two plants called "yellow-wreck" and "black-wreck," the former of which floats in water when cut, and hence, being more easily managed, is more commonly used in the Highlands than the other which does not float. The weed is cut only during spring-tides, and it is important to dry and burn it before it suffers from rain, as otherwise it is apt to ferment. Cutweed yields less iodine and potash than driftweed.

In Scotland the weeds are burned in kilns on level ground, 14 to 16 feet long by 2 feet broad, surrounded by a stone wall 8 to 10 inches high. The kiln is kindled with dry heath or straw, on which the dried seaweeds are placed, the laying on of the weed being done very carefully, so as not to allow it to burst into a flame. When this operation has been in progress from six to eight hours, a portion of the end walls is pulled down and the porous ash is worked up and kneaded until it melts and runs together, and thus forms the "floor," a cake from 3 to 6 inches thick. The whole operation is then proceeded with afresh, a second floor is formed &c. up to four and even six floors. The fused mass is broken up by throwing water upon it.

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In the north-west of Ireland the kelp is chiefly made from driftweed, which comes in during April and May; it is burnt in small heaps or holes, at a lower temperature, so that the kelp is more porous and much richer than that from the Western Islands.

On the west coast of France, in Normandy and Brittany, especially on the shores of La Manche, the "driftweed" has been collected from time immemorial. When the weed has been gathered or cut, it is dried, and afterwards put into stacks which stand until July or August, when it is burned in round or rectangular pits, which are protected on their sides and bottom by stones or plates. The pits are filled with dry weed and set on fire, fresh weed being continually added till the heat becomes so great as to soften and ultimately fuse the ashes.

These methods however are open to all the objections pointed out some years ago by Heinrich Rose, as applying to the older process of incinerating plants, the chief of which are, that, owing to the great heat applied, volatile substances, iodine and potassium-salts for example, are to a great extent lost, and that the carbon deoxidises the alkaline sulphates, reducing them to sulphites, hyposulphites, and even sulphides, which accumulate in the mother-liquor and require a large quantity of sulphuric acid to reconvert them into sulphates.

To obviate these objections, various plans have been proposed, consisting chiefly in charring the weeds only slightly before lixiviating, or in subjecting them to a distillation-process, whereby tar and illuminating gas are obtained, together with a residue of charcoal. This when lixiviated, yields a solution containing the soluble mineral constituents of the seaweed, which are thus obtained with much less loss than by the ordinary process. (See SEAWEED.)

*Composition of the Kelp and Varec.*—The differences in the kelp and varec from different localities are very great; not so much however when manufactured at the same place, as the great difference in the composition of the ash of the seaweeds, even of the same species, might lead one to expect. According to Golfier-Besseyre's analyses of French varec, the sulphate of potassium varies from 11 to 44 per cent., and in one case fell as low as 2 per cent.; the chloride of potassium from 12 to 35 per cent., and in one instance it was only 0·36 per cent.; the sulphate of sodium from 0 to 35 per cent.; the carbonate of sodium from nil to 17 per cent.; and the chloride of sodium from 9 to 70 per cent.

*Extraction of the Salts.*—The separation of the three principal salts contained in kelp, viz., the chloride and sulphate of potassium and the chloride of sodium, is based on the following facts:—1st. That common salt is nearly as soluble in cold as in hot water; 2nd. That chloride of potassium is more soluble in hot than in cold water; and 3rd. That sulphate of potassium is only slightly soluble in cold water.

The following table exhibits the solubilities of these three salts at $12\frac{2}{9}$° and 100° C. (54° and 212° F.).

| Salts. | Quantities dissolved by 100 pts. of water | |
|---|---|---|
| | at $12\frac{2}{9}$° C. | at 100° C. |
| Sulphate of potassium . . . . . . | 10·5 | 27·0 |
| Chloride of potassium . . . . . . | 32·0 | 59·4 |
| Chloride of sodium . . . . . . | 35·5 | 40·0 |

It must not, however, be forgotten that the *first solutions* of the potassium-chloride render the sulphate less soluble, whereas the sodium-chloride renders the potassium-sulphate more soluble in the *second lye* than in pure water.

In Scotland, the kelp broken into small pieces, is thrown into large cast-iron vats containing filters made of straw, dried seaweed, or small stones, and connected by pipes, so that the liquid may flow from one to the other. Water is poured into the first vat, filters through into the second, and so on, becoming continually more charged with the salts, and when saturated is made to flow into an underground receiver, whence it is run or pumped into the boiling-pans. When the liquor in a tank falls to 5° Twaddell, it is run off, and the tank is refilled with fresh kelp. At first the liquors stand at 50° T., but by the time the last vat is saturated, they fall to 35° T., below which strength no liquors are evaporated. The filters are renewed at every fifth operation. The exhausted mass, still containing some kelp, is sold to bottle manufacturers.

The kelp-liquor, from 35° to 50° T., is evaporated in iron pans, and boiled down to 60° T.; the salt, which falls in great quantities during the evaporation of the liquid, is an impure sulphate of potassium; it is regularly fished out, and thrown into a wooden vessel, with a perforated bottom. The liquor of 60° T. is allowed to settle and run off into a cooler, where the chloride of potassium crystallises out. These crystals are thrown into a basket, and allowed to drain. The mother-liquor is boiled up to 68° T., when sulphate, chloride, and carbonate of sodium salt out, and are drained in the same way as before. The liquor is allowed to cool again, and another crop of chloride of potassium is obtained. The mother-liquors are then run off, treated as before, and boiled up to 74° T., during which operation the same sodium-salts separate, and are fished out; the liquor again run into coolers, furnishes a third crop of chlorids of potassium. During the evaporation of the first liquor, the pan is occasionally fed with small quantities of kelp-liquor, but during the boiling of the second and third liquors, nothing but the corresponding mother-liquors are supplied. The salts separating during the boiling of the second and third mother-liquors are sold as kelp-salts, and contain on an average from 9 to 14 per cent. of alkali; they vary very much in composition, as the following analyses prove:

*Analyses of Kelp-salts* (Richardson).

| Salts. | 1. | 2. | 3. | 4. |
|---|---|---|---|---|
| Carbonate of sodium . . . . | 1·08 | 6·23 | 15·04 | 23·68 |
| Chloride of sodium . . . . | 80·65 | 69·97 | 64·69 | 41·17 |
| Sulphate of sodium . . . . | 10·03 | 4·70 | 15·27 | 17·91 |
| Sulphate of potassium . . . . | 7·47 | 10·43 | traces | trace |
| Chloride of magnesium . . . . | | | | |
| Insoluble matters . . . . . | | | | |
| Water . . . . . . . | 1·60 | 8·50 | 4·74 | 18·00 |
| | 100·83 | 99·83 | 99·74 | 100·76 |

The first crystallisation yields about 86 to 90 per cent., the second and third, 96 to 98 per cent. of pure chloride of potassium, whilst the fourth contains some sulphate of sodium.

In France the varec is sometimes ground, and the lixiviation is conducted in wooden tanks, with false (perforated) bottoms, in such a manner that the chlorides of potassium and sodium are first extracted, whilst the sulphate of potassium is obtained in the second lye. Fresh water or weak lye is run on the fresh kelp, and thence over kelp which has already been treated with water, &c., &c., until the density reaches 1·12 to 1·16. These lyes contain large quantities of the chlorides of potassium and sodium, whereas the sulphate of potassium is present only in small proportion. The residue is now treated similarly, until the lyes stand at 1·06, and contain principally sulphate of potassium.

The lye containing the alkaline chlorides, is concentrated up to 1·333; and the chloride of sodium deposited is fished out, and thrown into wooden hoppers above the pan. The salt thus obtained contains chloride and even sulphate of potassium; to remove these, it is thrown into wooden boxes with false bottoms, and whilst the lye from a previous operation is run upon it, a jet of steam is admitted below the false bottom; the whole mass is stirred, allowed to settle, and the liquor is drawn off. This operation is repeated until the solution stands at 1·27, when it is run off, and employed as above mentioned for another portion of salt. The potassium-salts are thus almost entirely removed, and the pure sodium-chloride is drained and gently dried.

To separate the chloride of potassium, the lye, free from common salt, and standing at 1·33, is drawn into coolers, where the chloride of potassium crystallises out, the mother-liquor retaining iodide of potassium in solution.

The sulphate of potassium is obtained from the second washings of the varec, as previously explained. When the lye is evaporated in flat iron pans, the sulphate separates in small crystals, which are drained, washed with lye, and then with cold water.

The sulphate and chloride of potassium thus obtained may be converted into nitrate by decomposing them with an equivalent quantity of nitrate of sodium (p. 100).

### III. From Sea-water, Brine-springs, and Salt-beds.

#### 1. From *Sea-water.*

Potassium occurs in sea-water as chloride and sulphate to the average amount of 0·257 pt. in 1,000. The extraction of these salts from sea-water has been carried on in the south of France for the last ten years by a process devised by Balard depending upon the natural advantages of the climate, namely a powerful summer's sun, and a sufficient difference of temperature between day and night. The sea-water is first left to evaporate during the summer, in shallow ponds or "salt-gardens," whereby a considerable quantity of common salt is obtained, mixed towards the last with sulphate of magnesium (see SODIUM, CHLORIDE OF). The mother-liquor having a density of 31° B is also passed into a series of shallow ponds, whereby another crop of common salt is obtained during the day, and during the night a mixture of sulphate of magnesium with a double sulphate of magnesium and potassium. The mother-liquors from these salts are run into other ponds, where another crop of crystals is obtained, consisting chiefly of a double chloride of potassium and magnesium, which when dissolved in water heated by steam yields chloride of potassium on cooling (p. 718).

The mixed magnesic and potassio-magnesic sulphates are redissolved and evaporated, whereby the double salt, $K^2Mg''S^2O^8.6H^2O$, is obtained, which is used in the manufacture of alum, and for the production of carbonate of potassium by Leblanc's process. The mother-liquor, containing only the Epsom-salts, is worked up in winter. (See SULPHATES.)

The salt-works of Baynas, covering a surface of about 370 acres, yield

200,000 cwts. of common salt.
1,200,000 cubic feet of mother-liquors at 31° B.
20,000 cwts. of summer-salts. { 11,000 cwts. of crystallised sulphate of magnesium.
9,000 cwts. of double-salts of { potassium. sodium. magnesium.
1,400,000 cubic feet of mother-liquors yielding in winter 90,000 cwts. of sulphate of sodium.

The produce just described is, however, attended with certain inconveniences, the chief of which are the loss of saline products by infiltration during the long sojourn of the concentrated liquids in the salt-gardens, and the redilution of these liquids by rain. These inconveniences are entirely obviated in the improved process of M. Merle, which consists in *salting down the concentrated sea-water by artificial refrigeration.* For this purpose the sea-water, after being concentrated in the salt-gardens to 1·24 specific gravity (28° B.)—at which degree of concentration it deposits about ⅛th of the sodium-chloride contained in it—is diluted with about 10 per cent. of pure water (to prevent too rapid deposition of sodium-chloride in the next stage of the process), and passed through a series of refrigerators constructed on Carré's principle (HEAT, iii. 98), in which the sulphate of magnesium and chloride of sodium are converted by mutual decomposition into chloride of magnesium and sulphate of sodium, the latter of which separates out. The mother-liquor still containing a considerable quantity of sodium-chloride is then run into boilers, where it is boiled down to 1·331 specific gravity (36° B.), and deposits nearly the whole of the sodium-chloride. The remaining mother-liquor containing the chlorides of potassium and magnesium, is passed into shallow coolers, where it deposits magnesio-potassic chloride, and from this the chloride of potassium is extracted by a process similar to that described on the next page.

### 2. *Brine-springs.*

The potash contained in these springs has not as yet been extracted on a manufacturing scale. Margueritte effects it by passing a current of hydrochloric acid gas through the mother-liquor left after the separation of the common salt. The whole of the potassium, whether it exists in the solution as magnesio-potassic chloride, or as sulphate, is then precipitated in the form of chloride. The passage of the gas is facilitated by keeping the liquid in constant agitation (see *Technology*, i. [3] 546). The method is likewise applicable to the preparation of potassium-chloride from the mother-liquor of sea-water, salt-marshes, &c.

The potassium may also be separated from such liquids by taking advantage of the action of lime on sulphate of magnesium, whereby the latter is converted into nearly insoluble sulphate of calcium. A milk of lime prepared with a strong solution of salt is added to the mother-liquor of salt-works, in sufficient quantity to decompose the sulphate of magnesium. The whole is boiled and allowed to settle; and the common salt is left to separate from the liquor in the usual salting pans, until the chloride of potassium begins to appear, when a small quantity of chloride of sodium and chloride of potassium crystallises out as the liquor cools. When the temperature falls to 140°—160° F., the liquor is run off into another cooler, where the chloride of potassium crystallises.

### 3. *Preparation of Potassium-chloride from the Salt-beds of Stassfurth.*

The occurrence of a deposit of magnesio-potassic chloride above the rock-salt of Stassfurth near Magdeburg, has been already mentioned (p. 607). The saline deposit, which is of great extent and thickness, is situated partly in the Prussian territory, partly in the Duchy of Anhalt. To the north of the town of Stassfurth, the saline deposits overlying the pure rock-salt have a thickness of 187 metres and may be divided into four principal layers, the limits of which are however not very well defined: 1. Immediately above the pure rock-salt is a bed 107 metres thick composed of layers of chloride of sodium interspersed with thin veins of *anhydrite*, $CaSO^4$.—2. Above this is a similar bed 31·5 metres thick, in which the anhydrite is replaced by *polyhalite*, $K^2Ca^2Mg(SO^4)^4.2H^2O$: in this bed also the chloride of sodium begins to be interspersed with small quantities of magnesio-potassic chloride.—3. *Kieserite bed*, 28 metres thick, consisting of layers of kieserite $MgSO^4.H^2O$, alternating with layers of magnesio-potassic chloride, the proportion of kieserite being greatest in the upper part. The average composition of this bed is 65 per cent. chloride of sodium, 17 kieserite, 16 magnesio-potassic chloride, and 2 anhydrite.

4. *Carnallite bed*, 20·5 metres thick, containing large quantities of carnallite $2KCl.MgCl^2.12H^2O$, especially in the upper part, alternating with rock-salt and kieserite. Its average composition is 55 per cent. carnallite, 25 rock-salt, 16 kieserite, and 4 hydrated chloride of magnesium. It contains also a few thin veins of *tachydrite*, $CaCl^2.2MgCl^2.2H^2O$, of *sylvine* or pure chloride of potassium, and tuberosities of *boracite*, $3MgO\,B^2O^3$, often enclosing nodules of carnallite or tachydrite. All the salts composing this bed are very deliquescent.

The composition of these beds, the most soluble salts occupying for the most part the highest positions, leads to the supposition that they have been deposited by the gradual drying up of an inland sea or salt-water lake; but their great thickness, and the occasional occurrence of veins of the less soluble in the midst of the more soluble salts, render it necessary to suppose that the waters of the lake were continually renewed, either by the products of the solution of neighbouring saline deposits, or by the waters of the ocean which formerly covered the plains of Northern Germany.

The percentage composition of pure carnallite and that of two specimens from Stassfurth as determined by analysis—*a*, by Rammelsberg (Pogg. Ann. xciv. 508); *b*, by Oesten (*ibid.* xcviii. 161)—is given in the following table; also the average composition of the "potash-salt" supplied to the works for the extraction of chloride of potassium.

| | Calculated. | Analyses. | | Average composition of "potash-salt." |
|---|---|---|---|---|
| | $2KCl.MgCl^2.12H^2O$ | *a.* | *b.* | |
| Chloride of potassium | 26·88 | 27·44 | 24·27 | 16 |
| Chloride of magnesium | 34·20 | 35·03 | 30·98 | 20 |
| Chloride of sodium | . . . | . . | 4·82 | 25 |
| Chloride of calcium | . . . | . . | 2·82 | |
| Sulphate of calcium (anhydrite) | . . . | . . | 1·05 | |
| Sulphate of magnesium | . . . | . . | . . | 10 |
| Ferric oxide, &c. | . . . | . . | 0·14 | 29 |
| Water | 38·92 | 37·53 | 35·92 | |
| | 100·00 | 100·00 | 100·00 | 100 |

The preparation of chloride of potassium from the "potash-salt" depends upon the fact that carnallite forms only in solutions containing excess of chloride of magnesium, so that when the salt is dissolved in hot water, and the solution is left to cool, no double salt separates, but the more soluble chloride of magnesium remains in solution, while part of the chloride of potassium crystallises out. The mother-liquors are then further treated for the recovery of the remaining quantity.

The "potash-salt" is first dissolved in cold water; the solution is heated by a steam pipe conveying steam at 120°, and continually stirred by revolving arms, to facilitate solution; and the liquid, after standing for ten hours, is decanted from the insoluble matter. The clear solution marking 32° B. is completely saturated with chloride of potassium and chloride of magnesium, and contains also small quantities of chloride of sodium and sulphate of magnesium. It is transferred to a series of crystallising vessels in which crystals are deposited containing from 60 to 70 per cent. chloride of potassium, a charge of 20,000 kilogrammes of "potash-salt" yielding from 16,000 to 17,000 kilogrammes of this impure chloride of potassium. The crystals are washed with water to remove the adhering mother-liquor and the chloride of magnesium, after which they contain 80 per cent. chloride of potassium.

The mother-liquors together with the wash-waters are concentrated to 36° B. Chloride of sodium is then deposited while chloride of magnesium and chloride of potassium remain in solution, and as the former is in excess, the solution on cooling deposits crystals of artificial carnallite, which are treated in the same manner as the original potash-salt.

The salt deposited during the concentration of the above-mentioned mother-liquors contains 65 per cent. chloride of sodium, 30 per cent. magnesio-potassic sulphate, $K^2Mg''(SO^4)^2.6H^2O$, and from 3 to 6 per cent. chloride of potassium. By washing it on cloth filters, about half the chloride of potassium is removed, and the wash-waters are used to dissolve a fresh portion of the "potash-salt."

The mother-liquors remaining after the deposition of the artificial carnallite contain 30·2 per cent. chloride of magnesium, 2·5 per cent. sulphate of magnesium, 0·2 chloride of sodium, 2·3 chloride of potassium. They were formerly thrown away, but are now used for the preparation of magnesium-salts.

The chloride of potassium sent into the market from the Douglas works at Stassfurth contains 82·00 per cent. pure chloride of potassium, 15·50 chloride of sodium, 0·50 sulphate of potassium, 0·50 sulphate of magnesium and 1·20 water. The last of these impurities is the most injurious in the several applications of the salt.

Other potassium-salts are also prepared at Stassfurth.—1. The chloride is converted into sulphate by double decomposition with sulphate of magnesium; but the mode of conducting the process is kept secret.

2. The sulphate is converted into carbonate of potassium by a process analogous to that of Leblanc for the manufacture of sodic carbonate (i. 792); but this branch of the manufacture has hitherto been carried out only on a small scale.

3. Saltpetre is prepared from the chloride of potassium by double decomposition with nitrate of sodium (see Nitrates, p. 100). (For further details see Joulin, Bull. Soc. Chim. 1865, i. 323, 401.)

The residue left on dissolving the crude potash-salt in water (p. 718) consists of 20 to 30 per cent. kieserite, $Mg''SO^4.H^2O$, 60 to 75 chloride of sodium, and 10 to 15 per cent. insoluble substances. It is used for the manufacture of sulphate of sodium. (See Sulphates.)

### IV. From Felspar and other Silicates.

Fuchs was the first to attempt the extraction of potash from the felspars and micas by calcining them with lime, and then lixiviating the frit. Numerous processes have been published since.

1. To obtain the alkali as hydrate or carbonate of potassium, Lawrence heats the mineral, throws it into water, and grinds it to a fine powder, which is mixed with damp sawdust, piled up in heaps, with alternate layers of straw, and watered now and then with urine or other nitrogenous liquids. These heaps are allowed to ferment during six months, then mixed with thick cream of lime, and made into bricks which are calcined at a high temperature. On lixiviation, the potash dissolves, whilst the silicate of calcium remains behind as residue.

In Hack's and Meyer's processes, which are similar to each other, an intimate mixture of 100 pts. of felspar and from 139 to 188 pts. of lime is heated for some hours at a temperature between a bright red and white heat, then ground to powder, and boiled from two to four hours under a pressure of eight atmospheres; a caustic lye free from lime and containing all the soda and from 9 to 11 per cent. of potash (of the weight of the mineral) is thus obtained. This lye is saturated with carbonic acid and evaporated, during which alumina and silica are first precipitated, after which the carbonate of sodium salts out, leaving the carbonate of potassium in solution.

F. O. Ward uses fluor-spar together with lime, and when the residue is to be employed in the manufacture of cement, adds a clay rich in alumina. The proportion of fluoride of calcium he recommends to be about 7 or 8 per cent. of the mixture, which is then calcined in a reverberatory furnace at a bright red heat, after which the mass is lixiviated in the usual manner; the liquor is boiled down, freed from the silica (about 25 per cent.) which precipitates on treating the liquid with carbonic acid, leaving carbonate of potassium in solution.

2. To obtain the alkali as sulphate or chloride of potassium, Tilghman mixes 2 pts. of felspar (containing 16 per cent. potash) with 1 pt. of lime and 1 pt. of sulphate of calcium or barium; grinds the whole to a fine powder; and heats the intimate mixture to bright redness for about eight hours, without fusion of the mass. The atmosphere of the furnace has to be carefully preserved in an oxidising condition by the admission of a sufficient quantity of air. The mass is then repeatedly lixiviated with hot water, and the solution of sulphate of potassium is evaporated (the sulphate of calcium or barium which deposits, being continually removed). To obtain chloride of potassium, ground potash-felspar and the chloride of either sodium, calcium or iron is heated for about six hours to bright redness in an iron cylinder, the heat being so

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regulated as to be above the melting point of the chloride employed, but below that of the felspar; the charge is raked into an iron vessel and immediately covered, until quite cool; the mass is then lixiviated, and the chloride of potassium obtained from the solution in the usual manner.

3. To obtain the alkali as potash-alum, Sprengel mixed the finely-ground mineral with strong sulphuric acid to the consistency of a thin paste, and left it thus for two months; on lixiviating the mass with a large quantity of water and evaporation a pure alum of the usual crystalline form was obtained. Turner employed sulphate of potassium instead of sulphuric acid, and mixed the ground felspar with its own weight of the sulphate. This mixture was thrown on the white-hot, inclined bed of a reverberatory furnace, and to the glass, which forms and flows to the sock of the furnace, carbonate of potassium, equal in weight to the sulphate used, was gradually added. This operation was repeated until the sock of the furnace was filled with glass. On boiling this glass with water, two-thirds of the silica in the felspar, in combination with part of the potash, was dissolved, and a porous mass was left, which, when boiled with dilute sulphuric acid of specific gravity 1·20 in leaden pans (160 lbs. of dry acid to every 285 lbs. of felspar), yielded a solution, which when concentrated, produced crystals of alum. To obtain carbonate of potassium from the above silicate of potassium liquors, they are treated with carbonic acid to precipitate the silica; to obtain caustic potash the same liquors are filtered through a bed of lime, which retains the silica.

None of these processes have however yet been carried out on the manufacturing scale; so that hitherto the immense stores of potash in the alkaliferous rocks have been only indirectly available for the purposes of industry, namely through the medium of plants, which extract the potash from the soil. Mr. Ward's process, called the "calcifluoric attack," seems however to hold out the best promise of success. The addition of fluor-spar greatly facilitates the decomposition of the silicate, and enables it to be effected at a temperature lower than would be necessary if lime alone were used; moreover the process yields the alkali at once in the caustic or carbonated state, whereas in most of the other processes in which an acid material has been added to facilitate the decomposition, the alkali has remained in combination with the acid, requiring a subsequent process of separation.

### V. Potash from Wool.

It is well known that sheep draw from the land on which they graze a considerable quantity of potash, which, after circulating in their blood, is excreted from the skin with the sweat. Chevreul pointed out that this peculiar compound, which the French call "suint," forms no less than a third of raw merino wool, from which it may be readily dissolved out by simple immersion in cold water. In ordinary wool it is less abundant, and according to MM. Maumené and Rogelet, the potassic sudorate or suint of ordinary wool forms on the average about 14 per cent. of the raw fleece. This compound is not a soap, as was formerly supposed, the grease of the wool (about 8½ per cent.) being in fact combined with earthy matter, chiefly lime, as an insoluble soap. The soluble sudorate is, according to Maumené and Rogelet, the potassium-salt of a peculiar animal acid containing nitrogen.

Maumené and Rogelet recover the potash from this compound on a manufacturing scale. The wool is placed in casks, pressed down as much as possible, and cold water is poured over it. No greasy particles escape with the brown solution, and all sand, &c. is retained by the wool, which acts like a filter. The solutions (of specific gravity 1·10) are boiled down to dryness; the sudorate, which has the appearance of baked molasses, is broken into lumps and calcined in retorts. The residue is lixiviated, and the liquors boiled up to 30° and even 50° B. The chloride and sulphate of potassium crystallise out on cooling, and the mother-liquor, when boiled down to dryness, yields carbonate of potassium, free from soda.

The production is generally 140 to 180 lbs. of dry sudorate of potassium, or 70 to 90 lbs. of pure carbonate, and 5 to 6 lbs. of sulphate and chloride of potassium from every 1,000 lbs. of raw wool. (See Hofmann's *Report on the Chemical Products in the International Exhibition of* 1862, p. 42.) T. R.

**POTATO.** *Solanum tuberosum.*—Potatoes (the tubers) contain, according to Henneberg, Ann. Ch. Pharm. lxix. 336), 0·34 per cent. nitrogen, and 75·80 per cent. water. A white variety analysed by Gronven (Jahresb. 1857, p. 520) exhibited the following composition: *a*, when grown with mineral manure; *b*, with manure rich in nitrogen.

| | Water. | Starch. | Protein substance. | Gum, Dextrin. | Sugar | Fat. | Extractive matter. | Cellulose. | Ash. |
|---|---|---|---|---|---|---|---|---|---|
| *a*. | 76·40 | 14·91 | 2·17 | 2·34 | 0·15 | 0·29 | 1·70 | 0·99 | 1·00 |
| *b*. | 75·20 | 15·58 | 3·60 | 1·29 | 1·11 | 0·31 | 1·99 | 1·03 | 0·90 |

According to **J. J. Pohl** (Wien. Akad. Ber. viii. 42; Jahresb. 1852, p. 811), the percentage of dry substance and of starch in potatoes varies with their specific gravity as follows:—

| Specific gravity. | Dry substance in 100 pts. | Starch in 100 pts. |
|---|---|---|
| 1·090 | 23·84 | 16·38 |
| 1·091 | 24·09 | 16·81 |
| 1·093 | 24·57 | 17·11 |
| 1·094 | 24·98 | 17·52 |
| 1·099 | 25·93 | 18·43 |
| 1·101 | 26·45 | 18·98 |
| 1·106 | 27·54 | 20·05 |
| 1·107 | 27·97 | 20·45 |
| 1·108 | 28·10 | 20·69 |
| 1·110 | 28·99 | 21·32 |
| 1·116 | 29·50 | 21·95 |
| 1·123 | 31·64 | 24·14 |

See also **Lüdersdorff** (Dingl. pol. J. lxv. 48), and **Von Balling** (*Gährungschemie*, ii. 54, and Suppl., p. 43; also **A. Vogel** (Chem. Centr. 1862, p. 334).

A ready method of determining the average specific gravity of a sample of potatoes is to throw a number of them (6 – 12) into a strong solution of common salt, and dilute the liquid with water till some of them sink in it, while others float. The dilute salt-solution has then the mean specific gravity of the sample, which may accordingly be determined by the hydrometer. (**Fresenius** and **Fr. Schulze**, J. pr. Chem. li. 436.)

On the nutritive value of potatoes, as compared with the tubers of other plants, see i. 350, 844; ii. 710.

*Ash of Potato-tubers* (**T. J. Herapath**, Chem. Soc. Qu. J. ii. 4).

| | "White apple." | "Prince's beauty." | "Axbridge kidney." | "Maggie." | "Forty-fold." |
|---|---|---|---|---|---|
| Ash in 100 pts. of the plant fresh | 1·30 | 1·06 | 1·27 | 1·09 | 0·88 |
| Ash in 100 pts. of the plant dried | 4·82 | 3·63 | 4·36 | 3·46 | 3·97 |
| Ash-constituents: | | | | | |
| A. Soluble: | | | | | |
| Carbonic anhydride . . . | 21·06 | 16·67 | 21·40 | 18·16 | 13·33 |
| Sulphuric anhydride . . . | 2·77 | 4·94 | 3·24 | 5·60 | 6·78 |
| Phosphoric anhydride . . | 5·72 | 8·92 | 3·77 | 6·67 | 11·43 |
| Potash . . . . . | 53·47 | 54·17 | 55·61 | 55·73 | 53·03 |
| Soda . . . . . . | trace | trace | trace | trace | trace |
| Chloride of sodium . . . | trace | trace | trace | trace | 2·09 |
| B. Insoluble: | | | | | |
| Calcic carbonate . . . | 0·84 | 2·05 | 3·02 | 1·95 | 2·29 |
| Magnesic carbonate . . . | 3·53 | 0·27 | 1·26 | 2·56 | 0·57 |
| Calcic sulphate . . . . | trace | trace | 0·12 | trace | trace |
| Tricalcic phosphate . . . | 3·36 | 0·68 | 3·83 | 5·37 | 2·86 |
| Trimagnesic phosphate . . | 9·25 | 12·30 | 7·55 | 3·54 | 7·62 |
| Basic ferric phosphate . . | trace | trace | 0·06 | trace | trace |
| Silica . . . . . . | trace | trace | 0·12 | trace | trace |
| | 100·00 | 100·00 | 99·98 | 99·58 | 100·00 |
| Soluble in water, per cent. . | 83·02 | 84·70 | 84·02 | 86·16 | 86·66 |
| Insoluble " " . | 16·98 | 15·30 | 15·96 | 13·42 | 13·34 |

See also analyses by **G. F. Walz** (Jahresb. 1850, Table C. to p. 661). For a comparison of the ash of healthy and diseased potatoes: **Griepenkerl** (Ann. Ch. Pharm. lxix. 354; Jahresb. 1849, p. 685); also **G. Kemp** (Chem. Gaz. 1847, pp. 69).

The following table exhibits the amount and composition of the ash of the stems and tubers of the potato, as determined by **Way** and **Ogston** (Journal of the Royal Agricultural Society, xi. [2] 529; Jahresb. 1850, Table C to p. 661); also of the tubers by **J. Moser** (J. pr. Chem. lxi. 321; Jahresb. 1853, p. 580), and by **Schulz-Fleeth** (Pogg. Ann. xcii. 266; Jahresb. 1854, p. 665); also by the latter, of the peel cut from boiled potatoes; of the residue (impure cellulose) obtained by washing the finely-ground potatoes on a sieve with water; and of the dried juice obtained by washing the ground tubers with water, filtering quickly, heating the liquid to coagulate the albumin, separating the clear juice therefrom, and evaporating.

*Composition (in 100 pts.) of the Ash of Potato-Stems and Tubers.*

| | | Potash, $K_2O$. | Lime, CaO. | Magnesia, MgO. | Ferric Oxide, $Fe_2O_3$. | Sulphuric anhydride, $SO_3$. | Silica, $SiO_2$. | Carbonic anhydride, $CO_2$. | Phosphoric anhydride, $P_2O_5$. | Chloride of potassium, KCl. | Chloride of sodium, NaCl. | Dry substance in 100 pts. | Ash per cent. | | Sulphur in 1,000 pts. of dry substance. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | In air-dried substance. | In substance dried at 100°. | |
| | I. Stems. | | | | | | | | | | | | | | |
| Way and Ogston. | Of flowering plants . . . . | 10·07 | 29·86 | 5·46 | 3·89 | 4·58 | 2·20 | 11·46 | 6·62 | 21·08 | 4·77 | 11·60 | 1·59 | 13·75 | |
| | Of plants after flowering . . | 11·44 | 37·02 | 6·00 | 3·78 | 5·12 | 8·22 | 14·09 | 2·27 | trace | 12·06 | 14·84 | 2·25 | 15·00 | 0·029 |
| | II. Tubers. | | | | | | | | | | | | | | |
| | Common round white :— | | | | | | | | | | | | | | |
| | From flowering plants . . | 50·88 | 4·50 | 5·70 | 0·29 | 1·70 | 5·46 | 10·97 | 18·10 | 5·01 | 0·29 | 9·28 | 0·66 | 3·45 | 0·035 |
| | From plants after flowering . | 50·93 | 3·76 | 3·87 | 2·11 | 3·31 | 1·12 | 7·30 | 17·68 | 8·98 | 0·88 | 11·66 | 0·60 | 2·76 | 0·043 |
| | From withered plants . . | 50·89<br>and 2·41 $Na_2O$ | 2·65 | 4·21 | 1·06 | 3·19 | 0·91 | 12·14 | 17·15 | 5·38 | . . | 17·06 | 0·71 | 2·98 | 0·063 |
| Moser. | Potatoes from Lombardy . . | 64·56 | 1·59 | 3·66 | 0·79 | 4·56 | 1·35 | . . | 17·55 | 1·10 | 2·91 | 23·97 | 1·04 | 4·33 | |
| | " " . . . | 63·55 | 1·80 | 4·28 | 0·45 | 3·92 | 0·24 | . . | 18·58 | 4·11 | 3·09 | 19·86 | 1·15 | 5·80 | |
| Schulz-Fleeth. | Round yellow . . . . . | 57·44 | 0·84 | 2·52 | 0·42 | 2·72 | 0·53 | . . | 16·67 | 18·34 | 0·53 | 31·36 | 1·225 | 5·03 | |
| | Light red . . . . . . | 51·71 | 1·13 | 4·13 | 0·51 | 6·45 | 1·25 | . . | 15·79 | 17·49 | 1·52 | 25·27 | 0·99 | 3·91 | |
| | Blue . . . . . . . | 55·30 | 1·00 | 4·63 | 0·33 | 3·00 | 1·00 | . . | 18·38 | 15·23 | 1·15 | 22·58 | 1·00 | 4·44 | |
| | Dark red . . . . . . | 63·06 | 0·51 | 4·59 | 0·38 | 2·42 | 0·26 | . . | 20·39 | 8·09 | 0·31 | 27·29 | 1·186 | 4·347 | |
| | Long yellow . . . . . | 64·59 | 1·57 | 3·25 | 0·53 | 2·93 | 0·63 | . . | 19·08 | 6·29 | 0·73 | 27·97 | 1·011 | 3·615 | |
| | Long red . . . . . . | 53·05 | 3·52 | 3·86 | 2·35 | 5·03 | 1·51 | . . | 25·50 | 3·86 | 1·34 | 31·05 | 0·55 | 2·631 | |
| | Round white . . . . . | 65·93 | 1·33 | 4·00 | 0·59 | 0·44 | 0·44 | . . | 14·97 | 12·15 | 0·14 | 23·67 | 1·047 | 4·423 | |
| | III. Peel. | | | | | | | | | | | | | | |
| | Of light red potatoes . . . | 72·86 | 7·27 | 7·01 | 2·40 | 0·40 | 1·95 | . . | 2·92 | 3·25 | 1·95 | . . | . . | 8·733 | |
| | Of blue potatoes . . . . | 68·10 | 8·89 | 6·04 | 3·02 | 0·43 | 3·45 | . . | 3·71 | 4·31 | 2·07 | . . | . . | 10·320 | |
| | Of round white potatoes . . | 69·56 | 12·72 | 7·02 | 3·07 | 0·35 | 2·65 | . . | 3·51 | 1·14 | | | . . | 9·724 | |
| | IV. Impure Cellulose.* | | | | | | | | | | | | | | |
| | From round yellow potatoes . . | 22·48 | 39·33 | 6·74 | 0·89 | ? | 2·47 | . . | 28·84 | 2·21 | | . . | . . | 2·47 | |
| | From light red potatoes . . . | 18·59 | 42·72 | 7·93 | 0·87 | ? | 4·45 | . . | 22·17 | 3·26 | | . . | . . | 4·45 | |
| | From long red potatoes . . . | 5·82 | 59·30 | 8·14 | 1·17 | ? | 3·49 | . . | 19·77 | 2·32 | | . . | . . | 3·49 | |
| | From round white potatoes . . | 8·51 | 50·00 | 7·45 | 1·06 | ? | 2·13 | . . | 27·66 | 3·19 | | . . | . . | 2·13 | |
| | V. Dried Juice. | | | | | | | | | | | | | | |
| | From round yellow potatoes . . | 60·32 | 0·95 | 2·70 | 0·32 | 3·17 | trace | . . | 14·44 | 18·10 | | . . | . . | 23·45 | |
| | From light red potatoes . . . | 58·92 | 1·05 | 4·72 | 1·18 | 3·59 | 0·11 | . . | 18·12 | 13·38 | | . . | . . | 36·48 | |

* See p. 721.

From experiments made by Nägeli and Zöller on the growth of potatoes, Liebig (Ann. Ch. Pharm. cxxix. 287) concludes that in a soil containing the average amount of nitrogen, ammonia may be dispensed with as a constituent of the manure for potatoes, without impairing the crop; that for a soil rich in potash, the addition of phosphates is absolutely necessary, and in a soil poor in potash (but containing a sufficiency of phosphoric acid) the addition of wood-ash is essential in order to ensure an increased production of the tubers. These experiments also showed that when potatoes are grown under otherwise equal circumstances, in peat, either in its natural state or manured with phosphoric acid and ammonia, two-thirds of them became putrid, whereas those grown in peat mixed with alkaline phosphates, carbonate of potassium, and gypsum were perfectly free from disease.

The juice of potatoes contains asparagin and malic acid (Hirsch, Ann. Ch. Pharm. li. 246; Ludwig, Arch. Pharm. [2] cvii. 10; Jahresb. 1861, p. 740). The aqueous extract of the tubers contains a glucoside soluble in alcohol. (Ludwig.)

On the potato-disease, see Jahresb. 1847—48, p. 1105; 1849, p. 704; 1850, p. 542.

**POTATO-FAT.** Fresh potatoes contain, on the average, 0·73 per cent. of fat extractable by ether, about half that quantity, but of different constitution, existing in the peel. When the juice of bruised potatoes, from which the starch has settled down, is heated to boiling, albumin and fat separate out, and the latter may be extracted by ether. Peeled potatoes thus treated, yield a comparatively light-coloured solid fat: unpeeled potatoes a dark liquid fat. By evaporating the ethereal solution, there are obtained from peeled potatoes: *a.* White, slender, stellate needles, which turn brown at 270°, without melting, are not saponifiable, resemble suberin, and contain, on the average, 71·34 per cent. C, 10·8 H, and 15·58 O.

*b.* The mother-liquor leaves when evaporated a yellow buttery fat, consisting of a mixture of fatty acids, free from glycerides, and easily soluble in aqueous carbonate of sodium. This fat melts at 42·5°, contains between 70·5 and 75·8 per cent. C, 10·7 and 11·7 H, and alters quickly in contact with the air. By saponification, decomposition with hydrochloric acid, and solution in aqueous alcohol, it yields crystals of fatty acids melting at 52°. On dissolving these in alcohol, and mixing the solution with a small quantity of neutral acetate of lead, thin laminæ crystallise on cooling, from which an acid melting at 50° may be separated. The mother-liquor mixed with a large quantity of neutral acetate of lead, yields the lead-salt of an acid melting at 58°. The acid melting at 50°, Eichhorn's *solanostearic acid*, is difficult to crystallise; its silver-salt contains 51·05 per cent. C, 8·86 H, 6·98 O, and 33·11 $Ag^2O$, agreeing approximately with the formula $C^{15}H^{29}AgO^2$. This, or a similarly constituted acid (73·79 per cent. C, 12·52 H, and 74·63 C, 13·09 H), is likewise obtained by the distillation of potato-fat. It is, according to Heintz, a mixture of palmitic and myristic acids.

*c.* Unpeeled potatoes, cut in slices, dried at 100°, pulverised and exhausted with alcohol, yield, after evaporation of the alcohol, an extract, from which ether dissolves a brown syrupy fat. On dissolving this in potash-ley, separating it out again with acid, and mixing it in alcoholic solution with ammonia and chloride of barium, barium-salts of the above mentioned solid fatty acids are precipitated, while Eichhorn's *solanoleic acid* remains dissolved, and may be obtained by evaporation as a viscid barium-salt, from which alcoholic hydrochloric acid separates the acid still coloured brown. This solanoleic acid is not converted into elaïdic acid by nitrous acid, and is but partially, or not at all, precipitated from its alcoholic solution by alcoholic neutral acetate of lead It occurs also, though in smaller quantity, in the fat of peeled potatoes. (Eichhorn, Pogg. Ann. lxxxvii. 227.)

**POTATO FUSEL-OIL.** See Fusel-oil (ii. 753).

**POTSTONE** or *Lapis ollaris*. A term applied to the coarser granular varieties of steatite, of dark colour, and more or less impure.

**POTTER'S CLAY.** See Clay (i. 1024).

**POTTERY.** See *Ure's Dictionary of Arts, Manufactures and Mines* (iii. 485—509).

**POUNXA.** Syn. with Borax.

**POURPRITE.** A blackish-red colouring matter contained in the sediment of old wines. It is insoluble in water, soluble in strong sulphuric acid, and is precipitated therefrom on addition of water; soluble in 150 pts. of alcohol of 80 per cent.; less soluble in stronger alcohol, quite insoluble in ether. (Batilliat, *Traité sur les Vins de la France.*)

**POWDER.** See Gunpowder.

**POWDER OF ALGAROTH.** Precipitated oxychloride of antimony (i. 327).

**POZZUOLANA.** *Pozzolana. Puzzolana.*—A volcanic product occurring near Pozzuoli between Rome and Naples; also in other countries in the neighbourhood of extinct volcanoes, in the Auvergne district for example. It is a grey or yellowish-brown mass, having a fine-grained or earthy fracture, and forms one of the best materials for mixing with lime for the preparation of hydraulic mortar, for which purpose it was used by the Romans. The Italian pozzuolana contains, according to Berthier, 44·5 per cent. silica, 15·0 alumina, 8·8 lime, 4·7 magnesia, 12·0 ferric oxide, 1·4 potash, 4·1 soda and 9·5 water.

**PRASE.** A leek-green variety of massive quartz.

**PRASEOCOBALT.** When dry roseo-cobaltic sulphate (i. 1053) is slowly heated to the melting point of lead, till it acquires a purple-lilac colour, the residue then dissolved in hot water, and the purple-red solution mixed with excess of hydrochloric acid, an orange-coloured precipitate is formed containing luteo-cobaltic sulphate and chloride, while the supernatant liquid contains luteo-cobaltic and purpureo-cobaltic chlorides, together with a leek-green crystallisable salt, the base of which, not yet examined, is designated by Gibbs and Genth (Jahresb. 1857, p. 237), as praseocobalt.

**PRASEOLITE.** A hydrous dichroïte from Bräkke in Norway (ii. 321).

**PRASIN.** A cupric phosphate from Libethen in Hungary, chemically identical with phosphochalcite (p. 661). (Church, Chem. News. x. 217; Jahresb. 1864, p. 862.)

**PRASOCHROME.** A dull green incrustation consisting of calcic carbonate coloured by chromic oxide, formed on the island of Scyro by the alteration of chromic iron. (Landerer, *Dana's Mineralogy*, p. 501.)

**PRECIPITATE.** This term is applied to any solid matter separated from a state of solution by the action of heat, light, or chemical reagents, in contradistinction to a deposit or sediment, which consists of solid matter merely suspended in a liquid, and settling down when left at rest. For the methods of collecting and washing precipitates, see DECANTATION (ii. 308), and FILTRATION (ii. 648).

**PRECIPITATE, WHITE.** A pharmaceutical name of certain ammoniacal chlorides of mercury; chloride of mercurammonium, $Hg''H^4N^2Cl^2$, being called fusible white precipitate, and chloride of dimercurammonium, $\overset{\prime\prime}{Hg}{}^2H^4N^2Cl^2$, infusible white precipitate (iii. 916).

**PRECIPITATE, RED.** Red oxide of mercury.

**PREDAZZITE.** A kind of bitter spar mixed with brucite from Predazzo in the Southern Tyrol. Hardness = 5. Specific gravity = 2·634. According to J. Roth (J. pr. Chem. lii. 346), it contains:

| | $CO^2$. | CaO. | MgO | $FeO^3$. $Al^2O^3$. | $SiO^2$. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|
| *a.* | 27·46 | 33·53 | 23·27 | 2·88 | 3·28 | 10·26 | = | 100·68 |
| *b.* | 33·35 | 46·67 | 14·54 | 0·48 | | 6·96 | = | 102 |

*a* may be represented by the formula $Ca''CO^3.Mg''H^2O^2$; *b*, by $2Ca''CO^3.Mg''H^2O^2$. (Dana, ii. 457.)

**PREGRATTITE.** A green, fine-scaly micaceous mineral from Pregratten in the Pusterthal. Specific gravity = 2·895. Hardness = 3. Contains, according to Oellacher (Jahresb. 1862, p. 747), 44·65 per cent. $SiO^2$, 40·41 $Al^2O^3$, 1·71 $K^2O$, 7·06 $Na^2O$, 0·84 FeO, 0·52 CaO, 0·37 MgO, 0·10 $Cr^2O^3$ and 5·04 water, whence Oellacher deduces the formula $2\left.\begin{matrix}\frac{6}{7}Na^2O\\ \frac{1}{7}K^2O\end{matrix}\right\}SiO^2.3(2Al^2O^3.3SiO^2)$, regarding the other constituents as adventitious. Kenngott, on the other hand, regards the water as essential. According to Rammelsberg, the mineral is probably identical with the paragonite of St. Gothard, which contains 46·81 per cent. $SiO^2$, 40·06 $Al^2O^3$, with a trace of ferric oxide, 0·65 MgO, 1·26 CaO, 0·40 $Na^2O$, with a trace of potash, and 4·82 water.

**PREHNITE.** *Koupholite. Edelite. Chiltonite.*—A hydrated silicate of aluminium and calcium, occurring in trimetric crystals, having the axes $a : b : c = 0·66963 : 1 : 1·19035$. Angle $\infty P : \infty P = 96° 56'$; $oP : P\infty = 146° 11\frac{1}{2}'$. Ordinary combination $\infty P . \infty\breve{P}\infty . \infty\bar{P}\infty . 6\breve{P}\infty . oP$; also with $6P$. $2P$, $\frac{2}{3}\bar{P}\infty$ and $\frac{3}{4}\breve{P}\infty$. Cleavage basal, distinct. The mineral occurs also reniform, globular, and stalactitic, with a crystalline surface, imperfectly columnar or lamellar structure, and strongly coherent; also compact granular or impalpable. Hardness = 6 to 6·5. Specific gravity = 2·8 to 2·953. Lustre vitreous, pearly on the basal faces. Colour light-green, passing into white and grey, often fading on exposure; streak uncoloured. Subtransparent to subtranslucent. Fracture uneven. Somewhat brittle. Pyroelectric. It gives off water when heated and melts before the blowpipe to a white or yellowish glass. Many varieties (koupholite) blacken when heated, and give off an empyreumatic odour, but ultimately burn white. It is slowly attacked by hydrochloric acid, but gelatinises easily therewith if previously ignited or fused.

*Analyses.*—*a.* From South Africa (Klaproth, *Rammelsberg's Mineralchemie*, p. 782).—*b.* From Mont Blanc: *Koupholite* (Walmstedt, Berz. Jahresb. v. 217).—c. Bourg d'Oisans in Dauphiny (Regnault, Ann. Min. [3] xiv. 154).—*d.* Dumbarton near Glasgow (Walmstedt).—*e.* Edelfors in Småland: *Edelite* (Walmstedt).—*f.* Radauthal in the Harz; in gabbro (Amelung, Pogg. Ann. lxviii. 512). -*g.* Rio des los Cipreses, Chile (Domeyko, Ann. Min. [4] ix. 3).—*h.* Niederkirchen, in Rhenish Bavaria: in the form of analcime (G. Leonhard, Pogg. Ann. liv. 479).—*i.* From the same locality, in the form of laumontite (Blum's *Leonhardite*) (Leonhard):

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* |
|---|---|---|---|---|---|---|---|---|---|
| Silica | 40·93 | 44·71 | 44·50 | 44·10 | 43·03 | 44·74 | 43·6 | 42·50 | 44·00 |
| Alumina | 30·33 | 23·99 | 23·44 | 24·26 | 19·30 | 18·06 | 21·6 | 30·50 | 28·50 |
| Ferric oxide | 5·66 | 1·39 | 4·61 | 0·74 | 6·81 | 7·38 | 4·6 | 0·04 | 0·04 |
| Manganous oxide | . . | 0·19 | . | . . | 0·15 | | | | |
| Lime | 18·33 | 25·41 | 23·47 | 26·43 | 26·28 | 27·06 | 25·0 | 22·57 | 22·29 |
| Potash | . . | . . | . . | . . | . . | . . | . . | 0·02 | 0·01 |
| Soda | . . | . . | . . | . . | . . | 1·01 | | | |
| Water | 1·83 | 4·45 | 4·44 | 4·18 | 4·43 | 4·13 | 5·3 | 5·00 | 6·00 |
| | 97·08 | 100·14 | 100·46 | 99·71 | 100·00 | 102·40 | 100·1 | 100·63 | 100·84 |

These analyses, neglecting the first, agree nearly with the formula $2(Ca''O.SiO^2).Al^2O^3.SiO^2.H^2O$, which requires 44·28 per cent. silica, 24·60 alumina, 26·82 lime and 4·30 water.

Prehnite occurs in granite, gneiss, and trap-rock, especially in the last. It was first found at the Cape of Good Hope by Colonel Prehn. Handsome polished slabs of it have been cut from masses imported from China. It sometimes occurs altered to green earth and felspar. (Dana, ii. 314.)

**PREHNITOÏD.** A mineral externally resembling prehnite, occurring in the hornblende rock between Kingsberg and the Solberg in Sweden. It melts before the blowpipe to a white enamel, and is easily attacked by acids. Contains, according to Blomstrand (J. pr. Chem. lxvi. 157), 56·00 per cent. silica, 22·45 alumina, 1·01 ferrous oxide, 0·18 manganous oxide, 7·79 lime, 0·36 magnesia, 10·07 soda, 0·46 potash and 1·04 water (= 99·36).

**PRIMULA.** The ash of the several parts of *Primula farinosa*, gathered near Ansbach in the summer of 1853, has been analysed under Wittstein's directions (Ann. Ch. Pharm. cviii. 203), with the following results:

| | Roots. | Leaves. | Stalks. | Flower-heads. | Entire plant. |
|---|---|---|---|---|---|
| Ash per cent. in the substance dried at 100° | 10·05 | 13·88 | 7·79 | 7·00 | 8·61 |
| Composition of the ash:— | | | | | |
| Potash | 2·13 | 17·10 | 26·63 | 27·30 | 22·24 |
| Soda | 17·86 | 7·41 | 6·85 | 3·90 | 7·68 |
| Lime | 21·90 | 21·84 | 17·36 | 11·94 | 17·94 |
| Magnesia | 4·06 | 10·45 | 8·00 | 8·71 | 8·21 |
| Alumina | 1·62 | 0·96 | 0·54 | 1·15 | 0·83 |
| Ferric oxide | 1·05 | 0·85 | 0·13 | 0·54 | 0·43 |
| Manganoso-manganic oxide | 1·92 | . . | . . | . . | 0·20 |
| Chlorine | 3·03 | 9·33 | 9·12 | 5·29 | 7·99 |
| Sulphuric anhydride | 2·28 | 5·01 | 1·31 | 5·46 | 2·77 |
| Phosphoric " | 3·28 | 3·78 | 6·68 | 8·41 | 5·98 |
| Silicic " | 2·53 | 8·05 | 5·11 | 10·79 | 8·64 |
| Carbonic " | 15·34 | 15·22 | 18·27 | 16·51 | 17·09 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The composition of the ash of the entire plant was calculated from that of the several parts.

**PRIMULIN.** A crystallisable substance obtained from the root of the cowslip, *Primula veris*. (Hünefeldt, J. pr. Chem. vii. 58.)

**PRINCE'S METAL.** An alloy of copper and zinc (ii. 47).

**PRINTING, CHEMICAL.** Under this head we shall treat of certain modes of printing depending on chemical action, namely lithographic and zincographic printing.

**Lithography** (from λίθος and γράφειν) is the art of drawing on stone; and lithographic printing is the taking of impressions from such drawing. Its invention is due to Alois Sennefelder, who was born at Prague in 1772, but practised his art chiefly in Munich.

The stone used in lithography is a fine-grained limestone containing about 97 per cent. of calcic carbonate, with small quantities of silica, alumina, and oxide of iron. These stones are found in considerable quantity along the banks of the Danube, near Pappenheim; the best qualities are procured from the quarry of Solenhofen. They resemble in their aspect the yellowish-white lias of Bath; they should be free from veins, fibres and spots, hard enough to be scratched only with difficulty by a steel point, and splinters breaking from them should exhibit a conchoïdal fracture. To render a stone fit to receive a drawing, its surface is ground with fine sifted sand and water.

The drawing is made with a crayon called *lithographic chalk*, composed of soap, wax, and tallow, with a quantity of lamp-black sufficient to give it a dark tint. Now when traces are made on the stone with this soapy compound, a double decomposition appears to take place between the oleate and stearate of sodium in the soap and the carbonate of calcium, resulting in the formation of oleate and stearate of calcium and carbonate of sodium. The fatty calcium-salts thus produced are insoluble not only in water, but likewise in oils, both fixed and volatile.

The drawing being completed, the stone is prepared for printing by a process called "etching," which consists in floating a mixture of gum-arabic and dilute nitric acid upon it, whereby the portions of the surface untouched by the grease become covered with an insoluble compound of gum and lime. The action in this part of the process is somewhat obscure, but it is probable that the nitric acid dissolves the superficial particles of the stone, and the resulting solution forms with the gum an insoluble gummate or metagummate of calcium (ii. 954). One thing is certain, that the gum becomes firmly fixed on the stone, and cannot be removed even by repeated washing with water. The nitric acid also acts upon the chalk by laying hold of the alkali, and setting the fatty acids free.

The stone thus prepared is next washed with water, to dissolve off the excess of gum and the nitrates of sodium and calcium, and afterwards with oil of turpentine, which removes the excess of grease from the drawing and renders it nearly invisible. The fatty calcium-salts formed by the action of the soap on the carbonate of calcium, are however insoluble in the turpentine and remain untouched; and on subsequently wetting the surface of the stone with water, and passing over it a roller covered with printing ink, composed of linseed oil and lamp-black (iii. 273), the ink adheres to those parts of the surface where these fatty salts are situated, while the remaining portion, which has been acted on by the gum, does not take up the printing ink, because the fatty acids of the linseed oil are incapable of decomposing the compound of lime and gum with which those portions are covered, and mechanical adhesion is prevented by the film of water on the surface. The drawing is thus brought to light again with all its original distinctness, and impressions of it may then be taken off on paper by passing the stone under a press.

This view of the lithographic process represents it as depending altogether on a series of chemical actions. It is, however, more commonly supposed that the fatty matter of the lithographic chalk simply adheres to, or is partly absorbed by, the porous surface of the limestone; that the parts thus penetrated readily take up the printing ink; and that the adhesion of the ink to the other portions of the surface is prevented by the interposition of a film of water. But if this explanation were correct, a plate of alabaster, or sandstone, or porous earthenware, or any other stone capable of receiving a granular surface, ought to be available for lithography as well as limestone, whereas it is well known that carbonate of calcium is the only kind of stone that will answer the purpose: moreover, the mechanical theory of lithography takes no account of the peculiar action of the gum, which appears to be an essential feature of the process.

Any kind of fine-grained limestone may be used for lithography; marble will yield impressions when treated as above; but its crystalline structure prevents it from taking the proper grain. The preference given to the stones of Solenhofen and the neighbouring localities is owing to the closeness of their texture and to their occurrence in slabs of every required thickness parted by regular seams, which renders the quarrying comparatively easy: stones requiring to be sawn into slabs would be too expensive.

We now proceed to give a short account of the various methods of writing or drawing upon stone intended to print from.

Chalk drawings are executed on a stone to which a granular surface has been given with a solid pencil (lithographic chalk), the active part of which consists, as already mentioned, of grease, or oleic and stearic acids. This chalk can be modified from hard to soft in different degrees, to allow of its being cut to a fine point, or in the softer state, to be used with cloth or leather stumps; it may also be dissolved in spirits of turpentine or alcohol, and applied to the stone with a brush.

Lithographic ink is but a modification of the chalk, made to flow more easily when dissolved in water, being intended to be used with fine steel pens or fine sable brushes, that will draw a hair line. In a pen and ink drawing these lines must be solid, that is drawn with the ink in its fullest density consistent with freely flowing from the pen; the same with the fine brush. The ink can also be dissolved in different degrees of density to produce with larger brushes, lighter or darker washes or tints.

The solid chalk or liquid ink may also be passed over the whole surface of a stone, so as to render every part attractive for printing ink, and the drawing is then worked out from the black by removing the chalk or ink with a sharp point that will make white lines (exposing the stone), or with a flat scraper, which on a grained surface will produce a gradation of tints.

*Engraving on stone.*—The stone when polished is first rendered non-attractive for grease, by preparing the surface with a solution of gum and nitric acid, and when it is dry, the lines are cut through this preparation with a sharp needle or diamond point, whereby the natural stone is exposed; oil or other fat is then made to enter the cut, rendering the line attractive for the printing ink, whereas it can be wiped off from the rest of the surface. The stone can also be drawn upon with a solution of gum and acid, to which some colouring matter has been added, to enable the draughtsman to judge of the effect. When the drawing is dry, liquid ink or chalk is passed over it, which will render the parts of the surface not covered by the gum attractive for the printing ink.

These examples will show in how many different ways fatty matter and gum can be made to combine with the lime of the stone, and how the lithographic process can be varied. It is to these peculiar advantages that Sennefelder's invention owes its wide-spread application, both for commercial purposes and as one of the handmaids of the fine arts.

*Composition of Lithographic Chalk.*

| | | |
|---|---|---|
| 32 | parts of | Beeswax. |
| 4 | „ | Tallow (purified). |
| 24 | „ | Soap. |
| 1 | „ | Nitrate of potassium, dissolved in |
| 8 | „ | Water. |
| 6 | „ | Lamp-black. |

*Composition of Lithographic Ink:*

| *for Pens.* | | | *for Brush.* | | |
|---|---|---|---|---|---|
| 32 | parts of | Beeswax. | 16 | parts of | Beeswax. |
| 18 | „ | Tallow (purified). | 16 | „ | Tallow (purified). |
| 16 | „ | Soap (Marseilles). | 16 | „ | Soap. |
| 32 | „ | Shellac. | 16 | „ | Shellac. |
| 4 | „ | Carbonate of sodium,* dissolved in | 4 | „ | Mastic. |
| 8 | „ | Water. | 4 | „ | Carbonate of sodium, dissolved in |
| 6 | „ | Lamp-black. | 8 | „ | Water. |
| | | | 6 | „ | Lamp-black. |

*Permanent Liquid Ink for Autographic writing:* 5 pts. of soap, 8 mastic, 10 shellac, 1 rosin, 1 lamp-black, 3 carbonate of sodium (rendered caustic and dissolved in 4 pts. water). Dissolve the whole in 16 pts. water, adding more water if necessary to make the ink flow easily. Autographic drawing or writing is executed on a prepared paper and then transferred to the stone.

**Chromolithography.** Drawing and printing in colours from stone. In this application of the art, the plates of limestone offer peculiar advantages, especially for the reproduction of the painter's work, as the various modes in which the drawing materials, as chalk, ink, gum, &c., can be applied to the surface of the stone enable the lithographer to approach very closely the effect and handling of a painting in oil or water colour.

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* Or better, the same quantity converted into caustic soda.

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For the production of a chromolithograph, a succession of impressions is applied to a sheet of plate-paper from a number of stones on which are drawn in analysis, as nearly as possible, the various colours and tones of the original of which the chromolithograph is intended to be a copy. One of the great difficulties of the process is that nearly everything has to be drawn with the ordinary saponaceous *black* chalk and ink.

To copy a picture or drawing, and to make all the different colours correspond, a careful tracing is made with lithographic ink upon transparent transfer paper, or upon a sheet of gelatin; this tracing is transferred to a stone called the "keystone," and from this stone impressions are taken which are set off in the press on as many stones as will be required, the number varying according to the subject, twenty and even thirty being found sometimes necessary to produce the proper effect. The printing in colours is effected in the same manner, and depends on the same principles, as the production of a black lithograph, the various pigments being ground up with thickened linseed oil, and the resulting oil-colour spread evenly upon the leathern rollers with which the drawing upon the stone has to be charged. To secure an exact adjustment of all the colours, the stone to print from and the sheet of paper to print upon, are accurately and securely fixed into a registering frame which forms part of the press.

**Zincography.** Fatty substances act upon zinc and other easily oxidable metals much in the same manner as upon limestone, forming salts which are insoluble in water. A drawing may be made on a zinc plate with the same chalk or ink that is used for drawing on stone, and the remaining parts of the surface may be rendered non-attractive for printing ink in a similar manner, excepting that the solution of nitric acid and gum used for the purpose must be mixed with a concentrated decoction of nutgalls. When the plate has been covered for a short time with this solution, the parts not constituting the drawing lose their metallic lustre and assume a brown tint, and in that state are incapable of taking up printing ink. The mode of printing is the same as from stone.

Other metals give similar results with more or less distinctness; but none are found to be so well adapted for chemical printing as the stone plates of Solenhofen.

M. H.

**PROPALANINE.** $C^4H^9NO^2$ = *Methalanine*, $C^3H^6(CH^3)NO^2$ = *Amidobutyric acid*, $C^4H^7(NH^2)O^2$ = *Oxybutyramic acid*, $\left.\begin{matrix}H^2\\(C^4H^6O)''\\H\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$ (R. Schneider, Ann. Ch. Pharm. Suppl. ii. 70; Jahresb. 1861, p. 459.)—A compound produced by heating bromobutyric acid with aqueous ammonia. It crystallises from alcoholic solution in stellate or furcate groups of small laminæ and needles, which when dry, yield a dazzling white satiny powder, unctuous to the touch. It is inodorous, has a sweet taste, and is neutral to vegetable colours. It dissolves in about 3·5 pts. water of medium temperature, is very slightly soluble in cold alcohol, and requires 550 pts. even of boiling alcohol to dissolve it; quite insoluble in ether. It is not decomposed by cold aqueous potash, but gives off ammonia abundantly when fused with hydrate of potassium. When cautiously heated in a tube, it melts and sublimes partly undecomposed; but when quickly and strongly heated, it turns brown and carbonises, emitting vapours which have an alliaceous odour and alkaline reaction.

Propalanine, like its homologues, unites both with acids and with bases. The *hydrochlorate*, $C^4H^9NO^2.HCl$, crystallises in tufts of very soluble, pointed needles; the *nitrate*, $C^4H^9NO^2.HNO^3$, in fern-like groups of silky needles, easily soluble in water and alcohol, and having an acid reaction. A solution of 2 at. propalanine in 1 at. sulphuric acid dries up to a viscid mass; but with twice that proportion of acid, the *neutral sulphate*, $(C^4H^9NO^2)^2.H^2SO^4$, is obtained in colourless, easily soluble, concentrically grouped needles.—A *lead-compound*, $C^8H^{16}Pb''N^2O^4.H^2Pb''O^2$, is obtained as a white, crystalline, sparingly soluble powder, by prolonged boiling of aqueous propalanine with lead-oxide.—The *silver-compound*, $C^4H^8AgNO^2$, obtained in like manner, crystallises on evaporation over oil of vitriol in small crystals which are quickly blackened by light, and decompose at 100°.

Schneider thinks it probable that propalanine may occur in the animal organism associated with leucine.

**PROPARGYLIC ETHER.** (Liebermann, Zeitschr. Ch. Pharm. 1864, p. 746.)—When tribromide of allyl is digested for some time with alcoholic potash, the alcohol distilled therefrom yields with ammoniacal silver-nitrate a white precipitate, containing $\left.\begin{matrix}C^3H^2Ag\\C^2H^5\end{matrix}\right\}O$, and regarded by Liebermann as the silver-salt of an ether to which he gives the above name. The silver-compound treated with a solution of iodine in iodide of potassium, yields an iodated oil, $\left.\begin{matrix}C^3H^2I\\ C^2H^5\end{matrix}\right\}O$, from which, by addition of iodine and of bromine, the compounds, $\left.\begin{matrix}C^3H^2I^3\\ C^2H^5\end{matrix}\right\}O$, and $\left.\begin{matrix}C^3H^2IBr^2\\ C^2H^5\end{matrix}\right\}O$, may be obtained. The corresponding methyl-compounds are formed in like manner.

**PROPHETIN-RESIN.** A resin obtained from *Cucumis Prophetarum*. (See Cucumis, ii. 172.)

**PROPIONAMIDE.** $C^3H^7NO = \left.\begin{matrix}C^3H^5O\\ H^2\end{matrix}\right\}N$.—Produced by the action of ammonia on propionate of ethyl. It is decomposed by heating with potassium, yielding cyanide of potassium, hydrogen, and carburetted hydrogen. By distillation with phosphoric anhydride, it is converted into cyanide of ethyl or propionitrile, $C^3H^5N = C^3H^7NO - H^2O$. (Dumas, Malaguti and Leblanc, Compt. rend. xxv. 657.)

*Hydrochlorate of Propionamide*, $C^3H^7NO.HCl$, is obtained, together with other products, by the action of moist chlorine on propionitrile (p. 736). It forms colourless crystals soluble in water and in alcohol, insoluble in anhydrous ether. When heated on platinum-foil, it volatilises, giving off irritating vapours. With platinic chloride, it yields chloroplatinate of ammonium. (R. Otto, Bull. Soc. Chim. 1865, i. 294.)

*Dichloropropionamide*, $C^3H^5Cl^2NO$.—Produced, together with dichloropropionitrile, by the action of dry chlorine on propionitrile. On subjecting the resulting liquid to the action of a freezing mixture, the dichloropropionamide separates in crystals which may be purified by pressure between bibulous paper, crystallisation from absolute alcohol, and sublimation. It then forms light nacreous scales, soluble in water, alcohol and ether, melting at 110·5° and solidifying at 86°. Its aqueous solution does not precipitate silver-nitrate. It dissolves without decomposition in ammonia and in hydrochloric acid; but on adding platinic chloride to its solution in absolute alcohol acidulated with hydrochloric acid, a precipitate of chloroplatinate of ammonium is formed, containing the whole of the nitrogen of the compound, and the filtered liquid, which has an odour of mint, deposits oily drops which solidify to crystals.

When dichloropropionamide is boiled in water with mercuric oxide, the latter dissolves, and the liquid on cooling deposits the compound $2C^3H^5Cl^2NO.Hg''O$, in nodules of hard white needles, soluble in boiling water and alcohol, nearly insoluble in ether, melting between 100° and 110°. (Otto, Rép. Chim. pure, iii. 257; Bull. Soc. Chim. 1865, i. 293.)

**PROPIONE.** $C^5H^{10}O = \left.\begin{matrix}C^3H^5O\\ C^2H^5\end{matrix}\right\}$ or $\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\}CO$.—Discovered by Frémy in 1835, and called by him *Metacetone*. It is sometimes called ethyl-propionyl, being the ketone of propionic acid. It is formed, together with other products, when sugar, starch, gum or mannite is distilled with excess of lime; also in the destructive distillation of lactate of calcium.

The following methods of obtaining it are more precise:—

1. Destructive distillation of certain propionates, *e. g.*, propionate of barium (Morley):

$$\underset{\text{Propionate of barium.}}{\left.\begin{matrix}2(CO.C^2H^5)\\ Ba''\end{matrix}\right\}O^2} = \underset{\text{Carbonate of barium.}}{\left.\begin{matrix}CO\\ Ba''\end{matrix}\right\}O^2} + \underset{\text{Propione.}}{\left.\begin{matrix}CO.C^2H^5\\ C^2H^5\end{matrix}\right\}}$$

2. Action of zinc-ethyl on chloride of propionyl (Freund and Pebal):

$$Zn''(C^2H^5)^2 + 2C^3H^5OCl = Zn''Cl^2 + 2(C^3H^5O.C^2H^5).$$

3. Action of carbonic oxide on sodium-ethyl (Wanklyn):

$$CO + 2NaC^2H^5 = Na^2 + CO(C^2H^5)^2.$$

Propione is a colourless mobile liquid, lighter than water and non-miscible with water, but freely soluble in alcohol and ether. Its smell resembles that of acetone. Boiling point 101°. It differs from many members of the ketone family in not being capable of forming a compound with acid sulphite of sodium.

According to Morley, boiling nitric acid converts it into propionic acid, there being neither nitropropionic acid nor acetic acid produced. According to Chancel, nitropropionic acid is formed by the action of nitric acid. Sulphuric acid and dichromate of potassium oxidise it to propionic, acetic and carbonic acids (Gottlieb). It is hardly attacked when dropped on potash in a state of fusion, there being traces only of propionate of potassium formed (Gottlieb). Propione is isomeric with valeral, but differs from it in its reactions. Unlike valeral, it gives no compound with alkaline sulphites and no valerianic acid when oxidised. J. A. W.

**PROPIONIC ACID.** *Metacetonic acid*, *Ethyl-formic acid*, $C^3H^6O^2$.—The third acid of the fatty series, discovered by Gottlieb in 1844 among the products of the action of caustic potash on sugar.

This acid is of little importance as a natural product. It is contained in crude oil of amber, also in cocoa-nut milk after it has turned sour, and in the distillate from some of the wines of the Bergstrasse (Gm. ix. p. 402). Béchamp (Compt. rend. liv. 1148) has found it in spoilt wine, together with acetic and lactic acid.

1. It is of interest as being the first organic acid, or indeed organic compound, obtained directly from carbonic anhydride. Carbonic anhydride and sodium-ethyl give propionate of sodium (Wanklyn, 1858):

$$CO^2 + NaC^2H^5 = \left.\begin{array}{c}CO.C^2H^5\\ Na\end{array}\right\}O.$$

2. It stands in intimate relation to lactic acid, being related to that acid in the same manner as acetic acid to glycollic acid. In order to render the connection between these compounds intelligible, the following formulæ are convenient:—

$$\begin{array}{cc}\text{Lactic acid.} & \text{Propionic acid.}\\ C^3\left\{\begin{array}{l}H^4\\ O''\\ (HO)\\ (HO)\end{array}\right. & C^3\left\{\begin{array}{l}H^4\\ O''\\ H\\ HO\end{array}\right.\end{array}$$

Propionic acid then is lactic acid in which one atom of peroxide of hydrogen has been exchanged for one atom of hydrogen. And lactic acid may be converted into propionic acid by first replacing one atom of its peroxide of hydrogen by chlorine, then replacing this chlorine by means of nascent hydrogen (Ulrich):

$$\begin{array}{ccc}\text{Lactic acid.} & \text{Chloropropionic acid.} & \text{Propionic acid.}\\ C^3\left\{\begin{array}{l}H^4\\ O''\\ (HO)\\ (HO)\end{array}\right. & C^3\left\{\begin{array}{l}H^4\\ O''\\ Cl\\ (HO)\end{array}\right. & C^3\left\{\begin{array}{l}H^4\\ O''\\ H\\ HO\end{array}\right.\end{array}$$

By using hydriodic acid, lactic acid may be at once converted into propionic acid. (Lantemann.)

3. A third general reaction for the production of propionic acid consists in the double decomposition between cyanide of ethyl (propionitrile) and water. This transformation may be effected either by boiling the cyanide of ethyl with potash-ley (Dumas, Malaguti and Leblanc), or with a mixture of 1 pt. of oil of vitriol and 2 pts. water (Frankland and Kolbe). Both these reagents cause the cyanide to decompose water:

$$C^3H^5N + 2H^2O = C^3H^5O.H.O + NH^3.$$

When potash is used, it reacts on the propionic acid and the ammonia is free; when oil of vitriol is used, it acts on the ammonia and the propionic acid is free.

4. A fourth general reaction which yields this acid is that of Harnitz-Harnitzky, who exposes hydride of ethyl and chloride of carbonyl (phosgene gas) to the action of sunlight, and obtains chloride of propionyl and hydrochloric acid:

$$COCl^2 + C^2H^6 = \left.\begin{array}{c}CO.C^2H^5\\ Cl\end{array}\right\} + HCl.$$

Chloride of propionyl and water give propionic acid.

5. A fifth general reaction is the oxidation of propionic aldehyde, which thereby becomes propionic acid:

$$\left.\begin{array}{c}C^3H^5O\\ H\end{array}\right\} + O = \left.\begin{array}{c}C^3H^5O\\ H\end{array}\right\}O.$$

It is worthy of remark that acetone, which is isomeric with propionic aldehyde, does not give propionic acid on being oxidised (Dumas and Gottlieb). Bromacetone, however, is converted into propionic acid (or perhaps isopropionic acid) by oxide of silver in presence of water:

$$2C^3H^5BrO + Ag^2O + H^2O = 2AgBr + 2C^3H^6O^2;$$

and acrylic acid $C^3H^4O^2$ is converted into propionic acid by simply taking up 2 at. hydrogen under the influence of sodium-amalgam. (Linnemann, Ann. Ch. Pharm. cxxv. 307.)

The foregoing methods of making propionic acid are examples of the five general methods of forming the acids of the fatty series. From the circumstance that common alcohol is the particular alcohol of which propionic is the derivative, and that so common an acid as lactic acid is the corresponding diatomic acid, it comes to pass that propionic acid is the best acid of the series for illustrating the employment of these general methods.

To the foregoing may also be added the method suggested by Kalle (Jahresh. 1861, p. 359), for converting the acids of the oxalic series into acids of the fatty series, namely, by distillation with hydrate of calcium. Succinic acid thus treated does in fact yield propionic acid, according to the equation $C^4H^6O^4 = C^3H^6O^2 + CO^2$; but the quantity obtained is very small, because the temperature at which the reaction takes place is very near to that at which the propionic acid suffers further decomposition, yielding first acetic acid, and afterwards carbonic anhydride and hydrocarbons.

There is also a number of special reactions which furnish propionic acid, but they yield it mixed with some of its homologues. When sugar, mannite, starch or gum is heated with caustic potash, there is formed propionate as well as acetate of potassium (Gottlieb). Metacetone, when it is oxidised with chromic acid, also gives propionic and acetic acids (Gottlieb). Redtenbacher has observed that when glycerin is treated with yeast and kept at 30° to 40° for some months, it yields propionic acid, little or no acetic acid, and traces of formic acid. In this process the free acid was neutralised from time to time. According to Döbereiner, glycerin gives this acid when it is exposed to the air in contact with platinum-black. Oleic acid distilled with nitric acid gives propionic acid and a great number of its homologues. Casein, fibrin, and vegetable fibrin distilled with peroxide of manganese and dilute sulphuric acid, give small quantities of propionic acid. The putrefaction of peas or lentils under water, the dry distillation of beeswax, the oxidation of the more volatile distillate from rape-oil by means of nitric acid, also the oxidation of turpentine by nitric acid, give propionic acid. The volatile oil of asafœtida and oil of mustard also yield this acid on oxidation. When citrate of lime is fermented with decaying cheese, or when sugar is fermented in contact with cheese and chalk, propionic acid is likewise formed (see Gm. ix. 403).

Lastly, propionic acid is formed by the action of hydriodic acid on pyroracemic acid (Wislicenus, Ann. Ch. Pharm. cxxvi. 225: Jahresh. 1863, p. 374):

$$C^3H^4O^3 + 4HI = C^3H^6O^2 + H^2O + 2I^2.$$

*Preparation.*—1. Metacetone, which is prepared by the destructive distillation of a mixture of sugar with lime, is allowed to run into a large retort containing dichromate of potassium and dilute sulphuric acid. When the effervescence caused by the formation of carbonic acid is over, the distillation is commenced; undecomposed metacetone goes over first, then the receiver should be changed, and the acetic and propionic acids collected. The separation of the acetic acid is managed thus. The mixed acids are neutralised with carbonate of sodium, and evaporated down to crystallise; whereupon the acetate of sodium crystallises out, leaving the propionate in solution. The propionate of sodium is finally distilled with sulphuric acid, whereupon propionic acid distils over. (Gottlieb, Ann. Ch. Pharm. lii. 121 *et seq.*).

A better way of separating the acetic acid is by the employment of Liebig's plan of fractional saturation (i. 250). The mixed acetic and propionic acids should be partly saturated with potash and then distilled; acetate of potassium then remains behind and propionic acid passes over.

2. It is, however, better to employ a process of preparation which does not involve the separation of homologues. The cyanide process answers very well. Cyanide of ethyl is added by drops to moderately strong potash-ley heated in a tubulated retort, the distillate being repeatedly poured back so long as it smells of cyanide of ethyl. The residue in the retort is then evaporated down to dryness and distilled with syrupy phosphoric acid (Dumas). (See also Williamson, Phil. Mag. [4] vi. 205.)

3. Now that both zinc-ethyl and sodium are tolerably cheap, the method of acting upon sodium-ethyl with carbonic anhydride has become quite practicable as a mode of preparation. The details of the operation are as follows:—Ten parts by weight of pure zinc-ethyl and one part of sodium are shaken up together; zinc then separates and sodium-ethyl dissolved in zinc-ethyl is produced. Mercury is next added; it takes up the finely divided zinc, and there result a lower layer containing zinc and mercury, and an upper layer of clear liquid which is sodium-ethyl together with zinc-ethyl. Carbonic anhydride is next passed into the apparatus, and combines with the sodium-ethyl; and the solid product of the reaction, after being treated with moist ether, and then with water, is finally evaporated to dryness and distilled with syrupy phosphoric acid or sulphuric acid.

Lautemann's method of decomposing lactic acid with hydriodic acid is also practicable as a mode of preparing propionic acid.

*Properties.*—According to Dumas, pure dry propionic acid is a solid at ordinary temperatures. It boils at 140°, and mixes with water in all proportions. Propionic acid floats on phosphoric acid or on solution of chloride of calcium. Redtenbacher, who obtained his acid by fermenting glycerin, maintains that propionic acid is not indefinitely soluble, even in water, but that when it is mixed with a little water, a portion of the propionic acid separates and floats on the aqueous solution of the acid. This observation requires confirmation, inasmuch as it is quite possible that Redtenbacher's acid contained traces of butyric acid or a higher homologue. The smell of the aqueous solution of propionic acid is very peculiar. J. A. W.

**Propionates.** $C^3H^5MO^2$ and $C^6H^{10}M''O^4$.—These salts are soluble in water and mostly crystallisable; according to Dumas, the alkaline propionates are unctuous to the touch.

The *ammonium-salt* is converted by phosphorous anhydride into propionitrile, $C^3H^5(NH^4)O^2 - 2H^2O = C^3H^5N$.—The *potassium-salt*, $C^3H^5KO^2$, forms white pearly laminæ. The *sodium-salt*, $C^3H^5NaO^2.H^2O$, dries up to an amorphous mass very soluble in water. An *aceto-propionate of sodium*, $C^2H^3NaO^2.C^3H^5NaO^2.\frac{2}{3}H^2O$, was once obtained by Gottlieb in delicate, shining, very soluble needles.

*Propionate of Barium*, $C^6H^{10}Ba''O^4$, crystallises in monoclinic prisms exhibiting the combination ∞P . ∞P∞ . oP . + P∞ . − P∞. Angle oP : + P∞ = 136° 4′; oP : − P∞ = 136° 32′; ∞P∞ : + P∞ = about 133°; ∞P∞ : − P∞ = 133° 35′; ∞P : ∞P = 97° 30′; ∞P∞ : ∞P = 131° 15′; + P∞ : ∞P = 116° 25′; −P∞ : ∞P = 117° 35′. (Provostaye, Compt. rend. xxv. 782). It is very soluble in water, and the solution yields, by spontaneous evaporation, large very regular crystals of a prismatic salt containing $C^6H^{10}Ba''O^4.H^2O$, which gives off its water at 100°. (Wrightson, Phil. Mag. [4] vi. 88.)

The *calcium-salt* crystallises by spontaneous evaporation in tufts of long prisms containing $C^6H^{10}Ca''O^4.H\,O$. They retain their water of crystallisation even when dried over oil of vitriol, but give it off at 100° (Wrightson). Strecker obtained the anhydrous salt in silky scales.

*Cupric propionate*, $C^6H^{10}Cu''O^4.H^2O$, obtained by neutralising the aqueous acid with carbonate of copper, forms very regular green octahedrons, sometimes with cube-faces. It dissolves in water with moderate facility, and is easily obtained in crystals by spontaneous evaporation. The crystals dried over oil of vitriol retain 1 at. water, which goes off at 100° (Wrightson). According to Nicklès (Compt. chim. 1849, p. 348), it crystallises in small oblique prisms very soluble in alcohol but very sparingly in water. Heated to 100° in a current of dry air, it gives off its water, together with a certain quantity of propionic acid. If from this point the temperature be suddenly raised to dull redness, the decomposition proceeds rapidly, with evolution of combustible gases which carry away a portion of the salt. The products of this distillation are: an odoriferous liquid composed of propionic acid and an oily body insoluble in water; carbonic anhydride and a hydrocarbon; and a residue of metallic copper and charcoal.

*Propionate of Lead.*—The solution of this salt, which has a sweet taste, dries up without yielding crystals, to a white mass, which when dried at 100° contains 63·4 per cent. oxide of lead (Frankland and Kolbe). According to Strecker, it forms needles containing $C^6H^{10}Pb''O^4.Pb''O$. This formula requires 77·5 per cent. lead-oxide.

Chloride of barium added to a tolerably concentrated solution of propionate of lead, forms at first a somewhat copious precipitate which disappears on agitation; if the addition of the chloride be continued, a point is at length attained at which the precipitate no longer redissolves; if the liquid be then filtered, and left to evaporate) chloride of lead separates at first, and afterwards magnificent limpid crystals which appear to belong to the dimetric system. They dissolve readily in water and produce gyratory movements on the surface of that liquid. They contain 4·15 to 3·88 per cent. chlorine, 35·96 to 35·70 lead, and 24·32 to 24·2 barium. (Nicklès, Ann. Ch. Pharm. lxi. 843.

*Propionate of Silver*, $C^3H^5AgO^2$, is obtained by adding nitrate of silver to the concentrated aqueous solution of the sodium salt as long as a precipitate is formed, boiling the precipitate in the liquid till it dissolves, whereupon some of the silver is reduced; and filtering at the boiling heat: the liquid then on cooling yields white, shining, heavy granules, which, when examined by the microscope, are found to consist of needles. The salt when merely exposed to light remains unaltered for several weeks; but at 100° it suffers partial decomposition and becomes black-brown. At a higher temperature, it melts quietly and burns away without noise (Gottlieb). When the precipitate is dissolved in boiling water, the greater part of it decomposes; and the crystals obtained from the solution decompose when heated, giving off acid vapours (Guckelberger). According to Frankland and Kolbe, it forms small crystalline laminæ, which either in the dry state or in solution, blacken when exposed to light or heated to 100°. It is less soluble in water than the acetate.

When propionic acid is warmed with carbonate instead of oxide of silver, an acid silver-salt appears to be formed, and crystals may be obtained containing $C^3H^5AgO^2.C^3H^6O^2$. (Wanklyn.)

*Acetopropionate of Silver*, $C^2H^3AgO^2.C^3H^5AgO^2$, is produced by boiling nitrate of silver with a mixture of acetate and propionate of sodium. The filtered solution on cooling deposits the double salt in arborescent groups of shining needles. The crystals may be dried at 100° without alteration; they do not melt at a stronger heat and are but slightly soluble in water. The solution blackens when boiled, from deposition of metallic silver.

Acetopropionic acid is also produced by the fermentation of calcic citrate in contact with putrefying curd. (How, Chem. Soc. Qu. J. v. 1; Gm. ix. 408.)

### *Substitution-derivatives of Propionic acid.*

**Bromopropionic acid,** $C^3H^5BrO^2$.—Produced: 1. By heating 1 at. propionic acid with 2 at. bromine to 150° for several days, and collecting the product which passes over on fractional distillation between 190° and 210° (Friedel and Machuca, Compt. rend. liii. 408; Jahresb. 1861, p. 379).—2. By the action of hydrobromic acid on lactic acid:

$$C^3H^6O^3 \quad + \quad HBr \quad = \quad C^3H^5BrO^2 \quad + \quad H^2O.$$

When lactic acid is heated to 180°—200° in a stream of gaseous hydrobromic acid, a small quantity of bromopropionic acid distils over; but a better mode of preparation is to heat lactic acid with rather more than an equal volume of cold saturated aqueous hydrobromic acid, in sealed tubes to 100° for several days, then agitate the product with ether free from alcohol and distil the ethereal solution. The portion which distils above 180° yields a large quantity of bromopropionic acid. Sometimes, however, carbonic oxide is formed at the same time together with a fragrant liquid which, when treated with alcoholic ether, yields a considerable quantity of ethylic bromopropionate. (Kekulé, Ann. Ch. Pharm. cxxx. 11.)

Bromopropionic acid prepared from lactic acid boils at 202° (corrected 205·5°) and solidifies at −17° to a radio-crystalline mass. It is converted by *sodium-amalgam* into propionic acid (Kekulé), and by boiling with *zinc-oxide*, into lactic acid (Friedel and Machuca; Kekulé). When heated with alcoholic *ammonia*, it yields alanine together with bromide of ammonium (Kekulé):

$$\underset{\substack{\text{Bromopro-}\\\text{pionic acid.}}}{C^3H^5BrO^2} \quad + \quad 2NH^3 \quad = \quad \underset{\text{Alanine.}}{C^3H^7NO^2} \quad + \quad NH^4Br.$$

An acid called *bromitonic acid*, having the composition of dibromopropionic acid, $C^3H^4Br^2O^2$, is produced by the action of bromine on citraconic acid in presence of excess of potash (Cahours). See CITRACONIC ACID (i. 993).

**Chloropropionic acid,** $C^3H^5ClO^2$.—This acid does not appear to be formed by the action of chlorine on propionic acid, but is obtained by the action of water on chloride of lactyl or chloride of chloropropionyl, $(C^3H^4O)''Cl^2$ or $C^3H^4ClO.Cl$ (iii. 466). It is less volatile than propionic acid, and smells like trichloracetic acid. Nascent hydrogen converts it into propionic acid (p. 730). Its *silver-salt*, $C^3H^4ClAgO^2$, is less soluble in water than the propionate, and is resolved by boiling with water into chloride of silver and lactic acid. The *lead-salt* decomposes in like manner (Ulrich, Ann. Ch. Pharm. cix. 271). The *barium-salt*, $C^6H^8Ba''Cl^2O^4$, evaporated with chloride of zinc, yields a *zinc-salt* having the properties of sarcolactate of zinc. (Lippmann, Ann. Ch. Pharm. cxxix. 81.)

Respecting *Chloropropionate Ethyl*, see PROPIONIC ETHERS.

**Iodopropionic acid,** $C^3H^5IO^2$. (Beilstein, Ann. Ch. Pharm, cxx. 226; cxxii. 366; Jahresb. 1861, p. 668; 1862, p. 244).—Produced by the action of iodide of phosphorus on glyceric acid. To prepare it, 52 cub. cent. of glyceric acid having a density of 1·26 are mixed with 100 grms. iodide of phosphorus (added in three separate portions), and as soon as the action, which may be allowed to go on with considerable energy, is complete, the residue is washed with ice-cold water, till the water runs off colourless, and the iodopropionic acid which remains is crystallised once or twice from boiling water. The portion remaining in the mother-liquor, may be extracted by ether free from alcohol, not by evaporation, as the aqueous solution is decomposed by heat. If ether containing alcohol is used, ethylic iodopropionate is produced.

Iodopropionic acid forms a dazzling white, nacreous, crystalline mass melting at 82°. It is easily soluble in hot water, very slightly in cold water. The mother-liquors of the acid, when slowly evaporated over oil of vitriol, deposit it in large, well-developed, apparently monoclinic crystals. The acid dissolves very easily in alcohol and ether, has a strong acid reaction, and decomposes carbonates. Hydrochloric acid gas passed into the alcoholic solution, converts the acid into the ethylic ether.

The salts of iodopropionic acid are converted by boiling with water into metallic iodide and hydracrylic acid (iii. 177):

$$\underset{\text{Iodopropionic acid.}}{4C^3H^5IO^2} + 3H^2O = \underset{\text{Hydracrylic acid}}{C^{12}H^{22}O^{11}} + 4HI.$$

**Nitropropionic acid,** $C^3H^5NO^4 = C^3H^4(NO^2)O^2$. (Chancel, Ann. Ch. Pharm. lii. 295.—Laurent and Chancel, [3] vii. 355; xiii. 462).—Produced as a heavy yellow oil by heating butyral or butyrone with nitric acid, and precipitating with water. It has an aromatic odour, a very sweet taste, is dissolved slightly by water, and in all proportions by alcohol. It remains fluid even at very low temperatures; is easily set on fire, and burns with a reddish flame.

The nitropropionates are generally yellow and crystallisable: they all, excepting the ammonium-salt, decompose with a kind of explosion when gently heated. Mineral acids decompose them, precipitating the oily acid.

The *ammonium-salt*, $C^3H^4(NH^4)(NO^2)O^2.H^2O$, may be sublimed without decomposition. It decomposes spontaneously when kept in a close vessel, yielding a gaseous and a liquid product. Sulphydric acid decomposes it, with precipitation of sulphur and formation of new products. The *potassium-salt*, $C^3H^4K(NO^2)O^2.H^2O$, is obtained in fine yellow scales by dissolving the acid in alcoholic potash. It gives off its water at 140°, and decomposes with explosion at a few degrees higher. It dissolves in 20 pts. water, but is nearly insoluble in alcohol.—The *copper-salt* is a dirty-green precipitate.—The *lead-salt* is a yellow precipitate.—*Silver-salt*, $C^3H^4Ag(NO^2)O^2.H^2O$. When a solution of the potassium-salt is mixed with nitrate of silver, a yellow precipitate is formed, probably consisting of a basic salt; for on boiling it with water, oxide of silver is deposited, and there remains in solution a silver-salt, which crystallises in rhomboïdal plates, and has the composition above indicated.

**PROPIONIC ALDEHYDE.** $C^3H^6O = C^3H^5O.H$. *Hydride of Propionyl. Metacetic Aldehyde. Propylaldid.*—This compound, discovered in 1847 by Guckelberger (Ann. Ch. Pharm. lxiv. 39), is produced: 1. Together with several other aldehydes and acids, by distilling casein, albumin, or fibrin with sulphuric acid and peroxide of manganese, or sulphuric acid and potassic chromate (Guckelberger).—2. Together with butyric aldehyde, by the dry distillation of a mixture of calcic formate and butyrate (Michaelson, Ann. Ch. Pharm. cxxxiii. 182).—3. Together with butyric aldehyde, propionic acid and butyric acid, by distilling tetrylic (butylic) alcohol with sulphuric acid and potassic chromate (Michaelson, *ibid.* cxxxiv. 69).

*Preparation.*—1. By distilling 1 pt. of dry casein with 3 pts. of peroxide of manganese, 4½ pts. oil of vitriol, and 30 pts. water. Skimmed milk is left to coagulate; the curd, freed as completely as possible from the whey by washing with water and pressure, is dissolved at 60° to 80° in dilute sodic carbonate; the solution is maintained at that temperature for some hours, the scum thereby formed being carefully removed; the slightly turbid liquid is precipitated by dilute sulphuric acid; the curd repeatedly stirred up with hot water, and the liquid each time pressed out of it, till the water runs away quite clear; and the resulting casein, which contains but a trace of fat, is dried.—4·5 pts. of oil of vitriol are next diluted with 9 pts water; the mixture is cooled to 50° or 40°; 1 pt. of dry casein, pulverised as finely as possible, is gradually added to it, with constant stirring, till, in the course of a few hours, it dissolves, and forms a brown or violet solution; and the remaining portion of fat, which then rises to the surface, is skimmed off. The solution, after standing for a day, is diluted with 10 pts. water, and introduced into a retort large enough to hold twice the quantity and containing 1½ pt. manganic peroxide; 11 pts. of water are added (making up the 30); the liquid is distilled into a well cooled receiver, as long as any odoriferous products pass over; 1½ pt. more manganese is introduced into the retort, together with a quantity of water equal to that which has already passed over; and the liquid is again distilled as long as the distillate has any odour.

The strongly acid and pungent distillate is neutralised with chalk, and distilled to one-half; and the resulting neutral distillate containing acetic, propionic, butyric, and benzoic aldehydes is redistilled into a well cooled receiver, collecting only the first portion which passes over, till this distillate presents the appearance of a milky water covered with yellow oil, becoming clear as it cools, and gradually depositing bitter almond oil. To separate the propionic aldehyde, the milky liquid is introduced into a retort or flask, to which is adapted a long tube slanting upwards at first, and afterwards conveying the vapours into the downwardly inclined condensing apparatus, and heated in the water-bath, at first only to 40° or 50°, at which temperature nothing but acetic aldehyde passes over, whilst the propionic aldehyde condenses in the upwardly inclined tube, and flows back again. The propionic aldehyde is then distilled over at 65° to 70°, the first portions still containing acetic aldehyde, whilst the last portions, which must be collected apart, are free from that impurity, and have a pleasant ethereal odour (at a higher temperature the butyral passes over, and above 100°, the bitter almond oil).

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The distillate collected between 65° and 75° is dehydrated over chloride of calcium, and redistilled, whereupon it begins to boil at 40°. The distillate collected between 50° and 70° is tolerably pure propionic aldehyde, not however exhibiting a perfectly constant boiling point.

The formic, acetic, propionic, butyric, valeranic, caproic, and benzoic acids, likewise formed by the oxidation of the casein, remain in the retort as calcium-salts after the volatilisation of the aldehydes. (Guckelberger.)

2. A mixture of 1 at. calcic formate and 1 at. calcic butyrate yields by fractional distillation a product which, after being neutralised by oxide of lead and dried by chloride of calcium, is resolved by fractional distillation into propionic aldehyde, boiling between 54° and 63°; butyric aldehyde passing over between 65° and 90°, and amounting to about two-thirds of the whole; and a small quantity of a liquid boiling between 48° and 53°. (Michaelson.)

3. When 12 pts. of pure tetrylic alcohol are added by small portions to a mixture of 20 pts. sulphuric acid and 15 pts. of acid potassic chromate dissolved in water, the mixture becomes hot and gives off carbonic anhydride, so that external heating is required only towards the end of the reaction. On distilling the product, propionic and butyric acids and aldehydes pass over below 100°, while a considerable portion of the alcohol remains unattacked; and on neutralising the acids with oxide of lead, dehydrating the liquid with chloride of calcium, and submitting it to fractional distillation, the propionic aldehyde, which constitutes the greater part of the product, passes over between 59° and 61°. (Michaelson.)

Propionic aldehyde is a limpid neutral liquid, having an ethereal odour. Sp. gr. = 0·79 at 15°. Boiling point between 55° and 65° (Guckelberger); 54° and 63° (Michaelson). Vapour-density, obs. = 2·111 (Guckelberger); 2·04 (Michaelson); calc. = 2·01. It turns acid slowly in the air, rather quickly in contact with platinum-black (Guckelberger). When heated to 100° with recently precipitated silver-oxide and a little water, it is converted into propionate of silver, with separation of specular metallic silver:

$$2C^3H^6O \quad + \quad 3Ag^2O \quad = \quad 2C^3H^5AgO \quad + \quad H^2O \quad + \quad Ag^4.$$

This character distinguished propionic aldehyde from acetone, with which it is isomeric. (Michaelson.)

*Tribromopropionic Aldehyde*, $C^3H^3Br^3O$.—A body having this composition is formed in small quantity, together with acid products, by the action of bromine on the alkaline salts of citraconic acid (i. 993). It is a neutral oil insoluble in pure water and in alkaline solutions; easily soluble in alcohol and ether; partially decomposed by heat. It is uncertain whether this body is a derivative of propionic aldehyde, or of acetone.

*Pentachloropropionic Aldehyde* or *Propionic Chloral*, $C^3HCl^5O$.—This compound occurs amongst the products obtained by distilling starch with hydrochloric acid and manganic peroxide. On saturating the crude distillate with chalk or sodic carbonate, and rectifying over a small quantity of calcic chloride, the propionic chloral passes over in the first portion of the distillate, together with an oily body, from which it may be separated by agitating the liquid several times with ice-cold water, decanting the solution when saturated, and heating it, the propionic chloral then seperating in heavy drops having a faint yellow colour. By diffusing these drops in a small quantity of water, and cooling to 0°, colourless rhombic tablets are obtained, which may be purified from adhering oil by pressing them in the cold between bibulous paper. They consist of a hydrate of propionic chloral, $C^3HCl^5O.4H^2O$. (Städeler, *Gerhardt's Traité*, ii. 434.)

**PROPIONIC ETHERS.** These compounds have not been much examined, the ethyl-compounds of propionic, bromopropionic acid, &c., being the only ones yet obtained.

*Ethylic Propionate*, $C^3H^5(C^2H^5)O^2$, is prepared by heating silver-propionate with a mixture of absolute alcohol and sulphuric acid, and is separated from the product by water, in the form of a liquid lighter than water and having a pleasant fruity odour. It is quickly decomposed by ammonia into alcohol and propionamide.

*Ethylic Bromopropionate*, was obtained by Kekulé, by treating with alcoholic ether the fragrant liquid sometimes produced in the preparation of bromopropionic acid by the action of hydrobromic acid on lactic acid (p. 733).

*Ethylic Chloropropionate*, $C^5H^9ClO^2 = C^3H^4(C^2H^5)ClO^2 = \left.\begin{matrix}C^3H^4ClO\\C^2H^5\end{matrix}\right\}O$, or *Ethylic Chlorolactate* $\left.\begin{matrix}(C^3H^4O)''\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\Cl\end{matrix}$ (A. Wurtz, Ann. Ch. Pharm. cvii. 192; cxii. 232; Ulrich, Chem. Soc. Qu. J. xii. 23).—This ether is produced, together with ethylic chloride and water, by the action of absolute alcohol on chloride of chloropropionyl (chloride of lactyl, iii. 646):

$$C^3H^4OCl^2 \quad + \quad 2C^2H^6O \quad = \quad C^5H^9ClO^2 \quad + \quad C^2H^5Cl \quad + \quad H^2O.$$

It is a liquid having a pleasant aromatic odour, a specific gravity of 1·097 at 0°, and distilling without decomposition at 150°. Vapour-density, obs. = 4·9 (Wurtz); calc. = 4·7. When heated with *sodium-ethylate*, it is converted into diethylic lactate (Wurtz, iii. 464):

$$\left.\begin{array}{r}(C^3H^4O)''\\ C^2H^5\end{array}\right\}\begin{array}{l}O\\ Cl\end{array} \quad + \quad \left.\begin{array}{c}C^2H^5\\ Na\end{array}\right\}O \quad = \quad \left.\begin{array}{c}(C^3H^4O)''\\ (C^2H^5)^2\end{array}\right\}O^2 \quad + \quad NaCl.$$

By the action of *nascent hydrogen* (zinc and dilute sulphuric acid) it is converted into propionic acid. (Ulrich.)

*Ethylic Iodopropionate*, $C^3H^4(C^2H^5)IO^2$.—Obtained by passing hydrochloric acid gas into an alcoholic solution of iodopropionic acid (p. 734). It is a colourless strongly aromatic liquid, heavier than water, soluble therein, and easily soluble in alcohol. It boils between 180° and 200°, and appears to volatilise without decomposition. (Beilstein.)

**PROPIONITRILE**, $C^3H^5N$, or *Cyanide of Ethyl*, $C^2H^5.CN$.—The formation, properties, and most of the reactions of this compound have been described under CYANIDES (ii. 211). The products obtained by treating it with chlorine have recently been examined by R. Otto (Ann. Ch. Pharm. cxvi. 195; Rép. Chim. pure, 1861, p. 257; Ann. Ch. Pharm. cxxxii. 181; Bull. Soc. Chim. 1865, i 293).

*Dry chlorine* passed into gently heated propionitrile, forms dichloropropionamide (p. 729), and dichloropropionitrile, $C^3H^3Cl^2N$, which may be separated by a freezing mixture, the former then crystallising out; and on submitting the remaining liquid to fractional distillation, dichloropropionitrile passes over between 104° and 107°.

Dichloropropionitrile is a limpid liquid having a disagreeable ethereal odour, insoluble in water, soluble in alcohol and in ether, decomposing in badly closed vessels. It burns with a smoky flame, emitting pungent vapours. When boiled with alkali, it gives off its nitrogen as ammonia, the last portions however going off very slowly, and yields, first chlorinated acids, then acids free from chlorine.

The residue left after the distillation of the dichloropropionitrile is a crystalline mass, having the same composition and probably consisting of a polymeric modification. It forms fine crystals or scales melting at 74·5°, subliming with partial decomposition, insoluble in water, melting in boiling water, and distilling over with aqueous vapour. It dissolves at 26° in 7·17 pts. of absolute alcohol, and in 0·77 pt. of ether. With alkalis and acids it behaves like the liquid modification.

The action of *moist chlorine* on propionitrile is very energetic, and is attended with rise of temperature, and the formation of a greater number of products. Propionitrile distils over holding in solution hydrochlorate of propionamide, which it deposits in crystals (p. 729); hydrochloric acid is evolved; sal-ammoniac is deposited; and if the action of the chlorine be continued, with cohobation, there finally remains a mass of crystals, which, when washed with cold water, and dissolved in absolute alcohol, yields first, small iridescent laminæ of a body A, having the composition $C^9H^{15}Cl^5N^2O^4$; then after the oily mother-liquid has been left for some time over oil of vitriol, crystals of a body B containing $C^9H^{14}Cl^6N^2O^4$; and finally, an uncrystallisable oil C.

The body A appears to be formed according to the equation:

$$3C^3H^5N \; + \; 5Cl^2 \; + \; 4H^2O \quad = \quad C^9H^{15}Cl^5N^2O^4 \; + \; 4HCl \; + \; NH^4Cl.$$

It melts between 166° and 168°; sublimes when cautiously heated; is insoluble in water, but soluble in alcohol and ether; and crystallises in small rhombic laminæ. Its solution in dilute hydrochloric acid forms a precipitate with platinic chloride, after standing for some time.

The body B melts between 151° and 152°, and in other respects resembles A.

The uncrystallisable oil C appears to consist of the body A, contaminated with other products of substitution. In contact with sodium-amalgam and water, it dissolves without evolution of hydrogen; and acids separate from the resulting liquid a yellowish mass, whose solution in dilute alcohol containing hydrochloric acid, yields, besides uncrystallisable mother-liquor, feathery crystals of a body D, which melts at 163°—164° and contains $C^9H^{26}Cl^8N^4O^8$.

The oil C distilled in a saltpetre-bath yielded a small quantity of dichloro-propionitrile containing hydrochloric acid, and a brown residue which solidified in a crystalline mass, and dissolved in absolute alcohol, leaving a slight residue of sal-ammoniac. This alcoholic solution deposited the three following crystallisable compounds, distinguished by their melting points and their solubility in alcohol:

|  |  | Melting point. |  |
|---|---|---|---|
| E. | $C^{18}H^{19}Cl^{6}N^{4}O^{6}$ | 189 to 191° | sparingly soluble. |
| F. | $C^{18}H^{24}Cl^{6}N^{4}O^{7}$ | 156 to 158° | more soluble. |
| G. | $C^{18}H^{23}Cl^{7}N^{4}O^{7}$ | 214 to 215° | from the mother-liquor. |

The action of moist chlorine on propionitrile in diffused daylight likewise gives rise to the formation of other compounds, but they are very difficult to separate.

When moist chlorine acts on propionitrile in direct sunshine, the resulting brown liquid deposits on standing, crystals of dichloropropionamide, and the liquid decanted therefrom yields by distillation, first water, hydrochloric acid and propionitrile, then (between 100° and 120°) dichloropropionitrile, and lastly (above 120°) dichloropropionamide, together with solid dichloropropionitrile (p. 736). In one experiment the liquid deposited after some time, cubic crystals, $C^{9}H^{14}Cl^{3}N^{3}O.3HCl.H^{2}O$, easily soluble in water and in alcohol.

**PROPYL** or **TRITYL**, $C^{3}H^{7}$. The third of the series of alcohol-radicles, $C^{n}H^{2n+1}$. (See TRITYL.)

**PROPYLAMINE.** See TRITYLAMINE.

**PROPYLENE.** See TRITYLENE.

**PROPYLIC ALCOHOL, ETHER, &c.** See TRITYLIC ALCOHOL, ETHER, &c.

**PROSOPITE.** A mineral occurring at Altenberg in the Erzgebirge in crystals, more or less altered to kaolin. The nucleus, if still unaltered, is colourless and transparent. Before the blowpipe it becomes white and opaque without fusing, and gives off water and hydrofluoric acid. It is decomposed by sulphuric acid. A colourless specimen of specific gravity 2·89 was found by Scheerer (Pogg. Ann. ci. 361) to contain 8·96 fluoride of silicon, 42·68 alumina, 22·98 lime, 0·31 manganous oxide, 0·25 magnesia, 0·15 potash, and 15·50 water (= 90·83), from which it is impossible to deduce a definite formula. According to Scheerer's measurements, the crystalline form of prosopite approaches nearly to that of heavy spar. Dana, on the other hand (*Mineralogy*, ii. 502), regards it as more nearly allied to datholite. Brush (Sill. Am. J. [3] xx. 273) found in violet-coloured crystals of so-called prosopite great diversity of form and composition. Some were violet and consisted of fluor-spar; others were white, soft and opaque, and consisted of a hydrated aluminic silicate.

**PROTAGON.** A name given by Liebreich to a substance believed by him to be the chief constituent of nervous tissue, from which cerebrin, myelin, &c. are developed. To prepare it, brain-substance, freed as much as possible from blood, is reduced to a pulp and treated with water and ether at 0°. From the remaining mass the protagon may be extracted by alcohol of 85 per cent. at 45°. On cooling the alcoholic solution to 0°, an abundant precipitate is formed which, after being well washed with ether and redissolved in warm alcohol, crystallises on cooling in acicular bundles.

Protagon is colourless, inodorous, scarcely soluble in ether, very soluble in warm spirit; with water it swells up to a gelatinous mass, which on further dilution becomes an opalescent fluid. Composition, $C^{116}H^{241}N^{4}PO^{22}$. Boiled with concentrated baryta-water, it is decomposed into glycero-phosphoric acid and a new base, neurine.

M. F.

**PROTEÏN** (πρωτεῖον, "pre-eminence") is the name given by Mulder to a product obtained by the action of potash on albuminoïds. He considers proteïn to be a definite compound forming the base of all the albuminoïds, and imagines that these bodies differ from one another only by varying quantities of *sulfimide* $(NH^{2})^{2}S$, and phosphimide $NH^{2}P$ (according to Mulder its formula $= C^{36}H^{25}N^{4}O^{10}$). This ingenious theory is, however, disproved by the fact that proteïn is not a homogeneous compound, as has been clearly shown by the experiments of Liebig and his pupils; in fact, it is nothing more than the albuminous substance more or less modified, and always contains a certain quantity of sulphur. For when an albuminoïd is dissolved at the common temperature in dilute potash, and the solution is saturated by an acid, the precipitate thus formed (proteïn) contains the whole of the sulphur, not a trace of which can be detected in the mother-liquid. If concentrated potash be employed, and the liquid heated, part of the sulphur is removed from the albuminoïd, and the solution being saturated with an acid, yields a proportionally smaller precipitate, still containing sulphur. Finally, if the whole of the sulphur be extracted from the albuminoïd, the alkaline solution yields no precipitates with acids (Laskowski). According to Fleitmann and Laskowski, the reaction takes place more rapidly in weak potash, if the liquid be heated with oxide of bismuth or silver. These oxides do not, however, remove all the sulphur. All the desulphurised matter appears to remain in solution.

The following are analyses of the so-called proteïn; they will be observed to differ very little from the composition of albumin.

|  |  | Dumas and Cahours, | Scheerer. |  | Fleitmann. |  |
|---|---|---|---|---|---|---|
|  | Mulder. | *fr. casein.* | *fr. fibrin.* | *fr. horn.* | By the action of oxide of bismuth on white of egg. |  |
| Carbon . . . | 54·6 | 54·4 | 54·1 | 54·7 | 53·8 | 54·1 |
| Hydrogen . . . | 6·9 | 7·1 | 7·0 | . . | 7·3 | 7·1 |
| Nitrogen . . . | 15·6 | 15·9 | 15·6 | . . | 16·2 | 15·9 |
| Sulphur . . . | . . | . . | . . | . . | 1·4 | 1·5 |
| Oxygen . . . | . . | . . | . . | . . | 21·5 | 21·5 |

*Oxyproteïn*, or binoxide of proteïn, is another of Mulder's compounds, the existence of which seems as little proved as that of proteïn. It remains insoluble when fibrin is boiled with water, and is supposed by Mulder to constitute the membrane of the red blood-cells, and to enter into the composition of the pellicle which separates from inflammatory blood (*Couenne inflammatoire*). According to v. Laer, it is also precipitated, after the proteïn, by the addition of an acid to the solution of horny matters in potash. Mulder found 53·1 per cent. C, 6·9 per cent. H, and 14·1 per cent N, and 0·7 per cent. S.

Mulder describes several other substances, which do not present the characteristics of pure compounds, *e.g. Trioxyproteïn* (an insoluble matter), *erythro-protide* (red extractive matter), *protide* (a bitter, soluble substance), *sulphoproteïc acid, gallotannate of proteïn*, and *chlorite of proteïn*.

(Mulder, J. pr. Chem. xvi. 129; xvii. 312, 315; Ann. Ch. Pharm. xxxi. 129.—Liebig, *ibid.* lvii. 132.—Fleitmann, *ibid.* lxi. 131.) C. E. L.

**PROTHEITE.** Syn. with VESUVIAN.

**PROTIC ACID.** An acid existing, according to Limpricht (Ann. Ch. Pharm. cxxviii. 185; Jahresb. 1863, p. 648), in the flesh-juice of the roach (*Leuciscus rutilus*) to the amount of 0·7 per cent. When the extract of the chopped flesh prepared with cold water is freed from albumin by boiling, the filtrate precipitated by baryta-water, evaporated after being freed from the precipitate, and again after standing for 48 hours, to allow the creatine to separate, and the remaining liquid cautiously mixed with an acid, it solidifies in consequence of the separation of a flocculent precipitate, consisting of protic acid. This acid is an amber-yellow brittle mass, only sparingly soluble in water, even at the boiling heat; its aqueous solution dries up to a gelatinous mass. It is moderately soluble in dilute acetic, hydrochloric, or sulphuric acid, more easily in aqueous ammonia, potash, soda, baryta, or lime. The acetic acid solution is not precipitated by ferrocyanide of potassium; the solution in ammonia or baryta-water gives precipitates with most metallic salts. Protic acid has nearly the composition of the protein-compounds. When boiled with dilute sulphuric acid, it yields a large quantity of leucine, but apparently no tyrosine. It has not been obtained from the flesh of warm-blooded animals or of herrings, or indeed of any fish excepting the roach.

**PROTORASTITE.** An augitic mineral occurring, with anorthite, on the eastern declivity of the Radanberg in the Hartz. It has a light brownish, or greenish to greyish-yellow colour, with a silky glimmer, and faint striation. Translucent, or in very thin laminæ, transparent. Exhibits two directions of cleavage inclined to each other at 134°, like augite. Hardness = 5—6. Specific gravity = 3·29. Very thin splinters melt before the blowpipe to a greenish-grey enamel. Two specimens gave by analysis the following results:

| $SiO^2$. | $Al^2O^3$. | $Co^2O^3$. | FeO. | MnO. | CaO. | MgO. | $H^2O$. | Chrome-iron. |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| 53·45 | 3·71 | 0·89 | 8·54 | 0·16 | 2·19 | 30·86 | 0·87 | 0·07 | = | 100·74 |
| 54·15 | 3·04 | . . | 12·17 | . . | 2·37 | 28·37 | 0·49 | . . | = | 100·59 |

The chrome-iron ore in the first specimen was mechanically mixed, and remained behind on treating the silica with potash. The ferrous oxide in the second specimen contained a small quantity of chromic oxide. The analyses show that the mineral is an augite $M^2O.SiO^2$, the silica being partly replaced by alumina. (A. Streng, Jahresb. 1861, p. 985; 1862, pp. 723, 793.)

**PROTOCATECHUIC ACID,** $C^7H^6O^4$.—An acid isomeric with oxysalicylic, carbohydroquinonic (iii. 214), and hypogallic acids (iii. 239), or perhaps identical with the latter. It is produced: 1. Together with oxalic acid, acetic acid, and humous substances, by the action of melted potash on piperic acid (p. 654):

$$C^{12}H^{10}O^4 + 8H^2O = C^7H^6O^4 + C^2H^2O^4 + C^2H^4O^2 + CO^2 + 7H^2.$$

On slightly supersaturating the fused mass with sulphuric acid, concentrating and boiling the residue with alcohol, a solution of protocatechuate of potassium is obtained. This solution is to be evaporated; the residue dissolved in water; the solution precipitated by neutral acetate of lead, the first portions of the precipitate, which are

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yellow, being rejected; and the white flocks subsequently precipitated, are to be decomposed by sulphydric acid. An aqueous solution is thus obtained, which, when evaporated, yields protocatechuic acid in furcate groups of crystals and laminæ. (Strecker, Ann. Ch. Pharm. cxviii. 280; Gm. xvi. 238.)

2. Catechin, which, according to Krant and v. Delden (Ann. Ch. Pharm. cxxviii. 285; Jahresb. 1863, p. 389), is isomeric with piperic acid [or rather differs from it by 1 at. water, having the composition $C^{12}H^{12}O^5$], likewise yields protocatechuic acid by fusion with potash.

3. Maclurin (morintannic acid, iii. 1049), fused with potash is resolved into protocatechuic acid and phloroglucin:

$$C^{13}H^{10}O^6 + H^2O = C^7H^6O^4 + C^6H^6O^3.$$

1 part of maclurin is evaporated in a silver basin with a solution of 3 parts potassium-hydrate, till the mixture becomes pasty; the mass is then acidulated with sulphuric acid, evaporated to dryness and treated with alcohol, which dissolves both the products of the reaction. The alcohol is then distilled off, and the aqueous solution of the residue is treated with neutral acetate of lead, which precipitates the protocatechuic acid, leaving phloroglucin in solution. The lead-precipitate is treated as above. (Hlasiwetz and Pfanndler, Ann. Ch. Pharm. cxxvii. 351; Jahresb. 1863, p. 595.)

4. By fusing guaiaretic acid, or purified guaiac-resin with potash. (Hlasiwetz and Barth, Ann. Ch. Pharm. cxxx. 346; Jahresb. 1864, p. 404.)

Protocatechuic acid crystallises from aqueous solution in furcate groups of crystals and laminæ (Strecker); in thin prismatic crystals (Hlasiwetz and Pfaundler); in tufts of needles belonging to the monoclinic system (Hlasiwetz and Barth). The crystals (air-dried) contain $C^7H^6O^4.H\ O$ and give off their 1 at. water at 100°. It dissolves in water, alcohol, and ether. The aqueous solution is coloured dark blue-green by ferric chloride, the colour changing to dark red on addition of alkalis. It reduces nitrate of silver with aid of heat, and on addition of ammonia, but does not reduce potassio-cupric tartrate [carbohydroquinonic acid separates cuprous oxide from the latter, iii. 215]. The dehydrated acid melts at 199°, and is decomposed by dry distillation into pyrocatechin (unmixed with hydroquinone) and carbonic anhydride: $C^7H^6O^4 = C^6H^6O^2 + CO^2$.

Maclurin (which is resolved by taking up the elements of water into protocatechuic acid and phloroglucin) is converted by nascent hydrogen evolved from sulphuric acid and zinc, into machromin $C^{14}H^{10}O^5$, a white uncrystallisable body, which quickly turns blue under the influence of air, light, heat, and oxidising agents. It is probably formed from protocatechuic acid, according to the equation,

$$2C^7H^6O^4 + H^4 = C^{14}H^{10}O^5 + 3H^2O.$$

By the action of hydrogen in alkaline solution, on the other hand, maclurin is converted into an uncrystallisable body $C^{14}H^{12}O^5$, probably formed from protocatechuic acid, as shown by the equation:

$$2C^7H^6O^4 + H^6 = C^{14}H^{12}O^5 + 3H^2O.$$

(Hlasiwetz and Pfanndler, Bull. Soc. Chim. 1865, ii. 147.)

The protocatechuates assume a fine violet colour when mixed with ferric salts *Protocatechuate of barium* forms crystals containing $C^{14}H^{10}Ba''O^8.5H^2O$ (Hlasiwetz and Pfaundler), and becoming anhydrous at 160° (Hlasiwetz and Barth). —The *calcium-salt* contains $C^{14}H^{10}Ca''O^8.4H^2O$ (Hlasiwetz and Pfanndler), $C^{14}H^{10}Ca''O^8.3H^2O$ (Hlasiwetz and Barth).—With solution of neutral acetate of *lead*, the aqueous acid forms white flocks of a basic salt, $C^{14}H^8Pb^2O^8.Pb''O.H^2O$, which dissolve in ammonia, potash, and acetic acid (Strecker). The latter solution when evaporated deposits colourless granules of the neutral salt $C^{14}H^{10}Pb''O^8.2H^2O$, which give off their 2 at. water at 140°, and dissolve with difficulty in acetic acid (Strecker). According to Hlasiwetz and Barth, the precipitated lead-salt contains $C^{14}H^{10}PbO^8.2Pb''O$.

**PROTO-COMPOUNDS.** The prefix *proto* was originally used to denote the first of a series of binary compounds arranged according to the number of atoms of the electronegative element. In this sense, cuprous oxide, $C\acute{u}^2O$, mercurous oxide $Hg''O$; and stannous oxide $Sn''O$, would be protoxides. At present, however, it is most commonly used to designate that compound in a series which contains 1 at. of the electronegative element, a sense which agrees with the former in most cases, but not in all; stannous chloride $Sn''Cl^2$ for example, is a dichloride according to the latter signification, a protochloride according to the former. (See NOMENCLATURE, p. 123.)

**PROTOGINE.** A granite occurring in Mont Blanc, consisting of quartz, orthoclase, oligoclase, talc, and mica. (Delesse, Bull. Soc. géolog. de la France [2] vi. 230.)

**PROUSTITE.** *Light red Silver ore. Lichter Rothgültigerz. Arseniksilberblende.*

A sulpharsenite of silver occurring in rhombohedral crystals, in which the principal axis of R = 0·8076, and the angle of the terminal edges = 107° 36′. The dominant faces are those of the scalenohedrons $R^3$ and $R^4$, combined with the prism ∞P2 and other faces. Cleavage tolerably distinct, parallel to R. Twins are of frequent occurrence. The mineral also occurs granular. Hardness = 2—2·5. Specific gravity = 5·422—5·56. Lustre adamantine. Colour and streak cochineal-red. Subtransparent to subtranslucent. Fracture conchoïdal to uneven. Before the blowpipe it gives off arsenical fumes and on charcoal ultimately leaves a globule of silver. Dissolves in nitric acid. Gives by analysis 19·51 per cent. sulphur, 15·09 arsenic, 0·69 antimony, and 64·67 silver, agreeing nearly with the formula $Ag^3AsS^3$ or $3Ag^2S.AsS^3$ (H. Rose, Pogg. Ann. xv. 472). Occurs in Saxony at Johanngeorgenstadt, Marienberg and Annaberg; at Joachimsthal in Bohemia; Wolfach in Baden; Markirchen in Alsace; Chalanches in Dauphiné; Guadalcanal in Spain; also in Mexico and Peru.

**PROVENCE OIL.** A name applied to olive oil obtained by cold pressure from the ripe fruits immediately after gathering.

**PRUNELLE SALT** or *Nitrum tabulatum.* Fused saltpetre.

**PRUNIN.** Syn. with BASSORIN. (See GUM, ii. 955.)

**PRUNNERITE.** A greyish-violet variety of limestone, from Faroe.

**PRUNUS.** *Plum.*—1. *Prunus domestica.*—The composition of several varieties of plum, as determined by Fresenius and others, is given under FRUIT (ii. 714, 715).

The fleshy part of mussel plums has been found by Payen (J. Pharm. [3] xvi. 279) to contain 12·99 per cent. water, 0·73 per cent. nitrogen (in the fresh substance), and 2·62 ash (in the dried substance). According to W. Tod (J. pr. Chem. lxii. 503; Jahresb. 1854, p. 665) fresh mussel plums contain 9·3 per cent. fleshy substance and 7 per cent. stone. When dried at 100°, the flesh gave 60·7 and the stone 30·9 per cent. water, 100 parts of the fleshy substance and of the stones, both in the fresh state, yielded the following quantities of inorganic constituents:

| | Soluble in water. | | | | | Insoluble in water. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | KCl | CaO | $K^2O$ | $SO^3$ | $P^2O^5$ | $Fe^2O^3$ | $Al^2O^3$ | CaO | MgO | MnO | $P^2O^5$ | $SiO^2$ | | |
| Flesh | . . | ·011 | ·173 | ·085 | ·003 | . . | ·003 | ·063 | ·010 | ·002 | ·055 | ·002 | = | ·407 |
| Stone | ·012 | ·026 | ·030 | ·021 | ·012 | ·014 | . . | ·124 | ·040 | ·001 | ·064 | ·036 | = | ·380 |

Faisst (Jahresb. 1852, p. 811), found in dried French mussel plums *a*, in Wurtemburg mussel-plums of the first quality *b*, and of second quality *c*, the following quantities of water, sugar, and acid:

| | *a.* | *b.* | *c.* |
|---|---|---|---|
| Water . . . . . | 32·2 | 27·9 | 27·9 per cent. |
| Sugar . . . . . | 48·1 | 56·3 | 47·6 „ |
| Acid . . . . . | 2·5 | 3·0 | 3·9 „ |

*Ash of Orleans Plums* (T. Richardson).*

| | Entire fruit. | Skin | Flesh | Kernel. | Skin of seed. |
|---|---|---|---|---|---|
| | | of fruit. | | | |
| Potash . . . . . . | 59·21 | 58·86 | 54·59 | 26·52 | 21·69 |
| Soda . . . . . . | 0·54 | 35·2 | 8·72 | 1·94 | 7·69 |
| Lime . . . . . . | 10·04 | 8·25 | 4·86 | 8·49 | 28·06 |
| Magnesia . . . . . . | 5·46 | 9·29 | 4·69 | 16·17 | 3·77 |
| Sulphuric anhydride . . . | 3·83 | 1·96 | 3·23 | 7·11 | 6·61 |
| Silicic „ . . . . | 2·36 | 0·81 | 3·15 | 2·38 | 2·57 |
| Phosphoric „ . . . . | 12·26 | 9·85 | 15·44 | 33·05 | 25·24 |
| Ferric phosphate . . . . | 6·04 | 7·45 | 4·80 | 3·83 | 4·37 |
| Chloride of sodium . . . | trace | . . | 0·62 | 0·49 | trace |
| | 99·74 | 99·99 | 100·10 | 99·98 | 100·00 |
| Ash per cent. . . . . . | 0·40 | 0·89 | 0·31 | 1·64 | 0·24 |

2. *Prunus Malaheb.*—The bark of this tree contains, besides the usual plant-constituents, an iron-greening tannin, an indifferent bitter principle, phlobaphene, coumarin and calcic oxalate. Dried at 100° it gave 11·2 per cent. ash, containing 6·79 per

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* Ann. Ch. Pharm. lxvii, Anhang zum 3te Heft; Jahresber. 1847-48, Tafel C zu S. 1075.

cent. $K^2O$ (with a little soda), 49·20 CaO, 3·44 MgO, 0·23 FeO, 0·04 Cl, 0·20 $P^2O^5$, 0·90 $SiO^2$, and 39·19 $CO^2$. (Kittel, Jahresb. 1858, p. 525.)

3. *Prunus spinosa.*—The Blackthorn or Sloe. Ripe sloes, treated successively with different solvents, yield 2·2 per cent. matter soluble in ether (iron-greening tannin, malic acid and calcium-salts, waxy fat, chlorophyll, and a small quantity of volatile oil); 4·8 per cent. matter soluble in *alcohol* (sugar, iron-greening tannin, malic acid and calcium-salts, red colouring matter, green resin); 4·3 per cent. matter soluble in *water* (gum, pectin, malic, sulphuric, and phosphoric acids, combined with potash, lime, and magnesia; extractive matter); 1·7 per cent. soluble in hydrochloric acid (ferric gallate, matter converted into humous substance, calcic and magnesic phosphates); 16·1 per cent. vegetable fibre (together with the stones, the kernels of which when treated with water yielded prussic acid); and 70·9 per cent. water. The colour of the ripe fruit is due to a purple-red substance separated on the inner surface of the skin, and agreeing in all essential characters with the red colouring matter of the grape. (J. B. Enz, Jahresb. 1857, p. 528).—According to Schreiner, *ibid.* 1856, 691), sloes contain malic acid, tartaric acid, and an iron-greening tannic acid. The fresh fruit yielded 65·4 per cent. water, and 0·72 per cent. ash, containing 3·48 $K^2O$, 4·3 $Na^2O$, 9·6 CaO, 6·2 MgO, 0·9 $Fe^2O^3$, trace of MnO, 0·5 $Al^2O^3$, 9·3 Cl, 1·8 $SO^3$, 10·5 $P^2O^5$, 7·0 $SiO^2$ and 24·1 $CO^2$.

**PRUSSIAN BLUE.** *Berlinerblau. Bleu de Prusse. Bleu de Paris.*—This well-known blue pigment consists essentially of hydrated ferric ferrocyanide, $Fe^7Cy^{18}.18H^2O = (Fe''')^4(Fe''Cy^6)^3.18H^2O$, generally mixed with varying quantities of potassio-ferrous ferricyanide, $KFe^2Cy^6 = (KFe'')Fe'''Cy^6$.—It was accidentally discovered in 1704 by Diesbach, a colour-maker in Berlin, who was preparing Florentine lake by adding carbonate of potassium to a decoction of cochineal mixed with alum and ferrous sulphate, and used for the purpose, an alkali over which the empyreumatic oil of blood had been rectified for the preparation of Dippel's animal oil. On examining the conditions of its formation, it was found that the blue colour could be produced by calcining blood with potash, and precipitating the ley thus obtained with ferrous sulphate. A more exact direction for its preparation was first given by Woodward of London in 1724. He deflagrated equal parts of tartar and saltpetre, calcined the residue with dried ox-blood, and precipitated the resulting alkaline ley with ferrous sulphate and alum, whereby a greenish precipitate was obtained, which turned blue when treated with hydrochloric acid.

Pure ferric ferrocyanide can be obtained by only one process, namely, by mixing a ferric salt with solution of ferrocyanide of potassium, keeping the former in excess, then washing and drying the precipitate. The product thus obtained, which has a splendid dark blue colour, is often called *Paris blue.*

For preparation on the large scale, however, it is customary to use, instead of a pure ferric salt, a solution of ferrous sulphate (copperas) which has been partially oxidised by exposure to the air, and subject the resulting bluish-white precipitate to the action of oxidising agents. The product thus obtained is, as already observed, a mixture of ferric ferrocyanide with potassio-ferrous ferricyanide (ii. 228). A common mode of proceeding is to mix solutions of 100 pts. ferrocyanide of potassium and 80 ferrous sulphate at the ordinary temperature, wash the precipitate with water; heat it with water to the boiling point, add 30 pts. *nitric acid* of 28° Bm., and from 15 to 30 pts. oil of vitriol, then wash the precipitate and dry it by heat. (Gentele, Dingl. polyt. J. lxi. 452.)

This process does not, however, yield a very fine blue. A better product is obtained by oxidising the white precipitate: *a.* With *nitro-muriatic acid.*—*b.* With *ferric chloride*, which is thereby reduced to ferrous chloride, and may be used again for precipitating a solution of the ferrocyanide. The solution of ferric chloride may be prepared by digesting red or brown hæmatite, free from lime and clay, or the basic ferric sulphate obtained as a residue in the preparation of Nordhausen sulphuric acid, in crude hydrochloric acid. The white precipitate, after filtration, and while still of a pasty consistence, is heated in a copper vessel to the boiling heat, then quickly turned out into a tub, and well mixed by stirring with the solution of ferric chloride till it has acquired its full depth of colour. The liquid, which contains ferric as well as ferrous chloride, is separated by filtration or decantation, and digested with pieces of iron to reduce it completely to ferrous chloride.

*c.* By a solution of *manganic chloride*, which is thereby reduced to manganous chloride. The economy of this method depends upon local circumstances. As the commercial value of manganese-ores depends upon the proportion of peroxide, $MnO^2$, which they contain, and in the common ores this oxide is often mixed with a considerable quantity of manganic oxide, which may be extracted by cold hydrochloric acid in the form of manganic chloride, this treatment may be applied so as actually to increase the value of the ores (that is, their chlorine-producing power), and at the same time obtain a solution adapted for converting the white precipitate into Prussian blue.

*d.* By *chromic acid.*—The white precipitate is heated to the boiling temperature, and mixed with an oxidising liquid prepared by dissolving 10 pts. dichromate of potassium in 10 pts. hot water, and adding to it when cold 13½ pts. oil of vitriol, till it has acquired its full depth of colour. The chromic acid is thereby reduced to chromic oxide, a compound which possesses considerable value as a colouring matter.

Whatever be the oxidising agent used, it is essential to the production of a fine colour that the white precipitate be converted into Prussian blue entirely by its agency, and not by atmospheric oxidation. For this reason the ferrous sulphate must be as free as possible from ferric salt, which end is best attained by placing some scraps of metallic iron in the vessel in which the solution is left to clarify before use, by which also any copper that it may contain is precipitated; and the white precipitate, as soon as formed, must be filtered as quickly as possible, and immediately subjected to the action of the oxidising liquid. (Wagner's *Jahresbericht der Chemischen Technologie,* 1855, p. 88.)

Common or *basic* Prussian blue is an inferior article prepared by the following process, which is the oldest of all the methods. A solution of 1 pt. ferrous sulphate and 2 to 4 pts. alum is precipitated by solution of ferrocyanide of potassium prepared as described under CYANIDES (iii. 231), and the dark-coloured precipitate, consisting of a mixture of alumina, ferrocyanide of iron and potassium, and hydrated sulphide of iron, is washed with cold water, till by the action of the air, the sulphide of iron is converted into ferrous sulphate, and washed away, and the potassio-ferrous ferrocyanide is converted, with loss of ferrocyanide of potassium (ii. 228), into Prussian blue. The chief use of the alum is to saturate the free alkali contained in the crude solution of the yellow prussiate, and prevent it from forming a precipitate of oxide of iron, which by its red-brown colour would spoil the blue. The precipitated alumina renders the blue paler, but on the other hand, it adds to the weight of the product. Prussian blue thus prepared may be freed from the greater part of the alumina, basic ferric sulphate, potassium-salts, and other impurities, by digestion with dilute sulphuric acid, and subsequent washing (Turner); or by dissolving it in strong sulphuric acid, precipitating with water, then digesting it in hydrochloric acid, and again washing with water. (Berzelius, *Lehrbuch.*)

Attempts have been made to utilise the waste lime and lime-liquors of gas works for the preparation of yellow prussiate and Prussian blue. This gas-lime contains cyanide of calcium and cyanide of ammonium, as well as free ammonia. The latter is expelled by the action of steam; the residue is lixiviated with water; and the solution, which contains the cyanides, is converted by addition of iron-salts into ferrocyanides and Prussian blue. A patent for this use of gas lime was taken out in this country by Mr. Spence in 1837, and a similar process was patented in France by Krafft in 1835 (Dingl. polyt. J. cxxxv. 393). According to Krafft, 1,000 pounds of gas-lime may be made to yield from 12 to 15 pounds of Prussian blue and 15 to 20 pounds of ammonia-salts.

According to Pohl (J. pr. Chim. lxiii. 382), Prussian blue is sometimes adulterated with starch turned blue by iodine. This (somewhat improbable) adulteration may be detected, if in large quantity, by the smell of hydriodic acid emitted on boiling the substance with water, and if in smaller quantity, by holding in the mouth of the test-tube in which the Prussian blue is boiled, a strip of starched paper moistened with very dilute hydrochloric acid; if iodine is present the paper will be turned blue. Prussian blue is sometimes also adulterated with chalk, gypsum and clay.

*Properties.*—Pure Prussian blue has a very dark blue colour. It usually occurs in hard brittle lumps having a coppery lustre and conchoïdal fracture. It is very hygroscopic, inodorous, tasteless and not poisonous. When contaminated with alumina, clay, &c., it has a paler colour and more earthy fracture. As a pigment, Prussian blue possesses great body and covering power. It is extensively used both alone and mixed with other colours. With chrome-yellow it forms a delicate green called *green cinnabar.* Respecting the reactions of Prussian blue, see CYANIDES OF IRON (ii. 228).

**PRUSSIC ACID.** Syn. with HYDROCYANIC ACID and CYANIDE OF HYDROGEN (ii. 214).

**PRUSSIN** or *Prussian.* A name applied by Graham to a hypothetical radicle, $C^6N^3 = Cy^3$ or Pr, polymeric with cyanogen, which may be supposed to exist in the ferro- and ferricyanides; *e.g.* [Fe = 28], ferroprussic acid = $(H^2Fe)Pr$; ferricyanide of potassium, $(K^3Fe^2)Pr$, &c. &c.

**PRZIBRAMITE.** A name sometimes applied to blende, $Zn''S$; also to a variety of göthite, $Fe^2O^3.H^2O$, called also *sammet-blende*, both of which occur at Przibram in Bohemia.

**PSATYRIN.** Syn. with HARTIN (iii. 14).

**PSEUDO-ACETIC ACID.** Syn. with BUTYRACETIC ACID (i. 688).

**PSEUDO-ALBITE.** Syn. with ANDESIN (i. 291).

**PSEUDO-ALKANNIN.** Syn. with ANCHUSIN (i. 290).

**PSEUDO-APATITE.** Opaque crystals of partially decomposed apatite from the Churprinz mine near Freiberg.

**PSEUDOBUTYLIC ALCOHOL.** See TETRYLIC ALCOHOLS.

**PSEUDOCHRYSOLITE.** A green obsidian from Moldanthein in Bohemia.

**PSEUDOCERAÏN.** A name given by Warington and Francis to an amorphous neutral fatty substance obtained by saponifying beeswax with potash, and precipitating with an acid. (Handw. d. Chem. vi. 682.)

**PSEUDOCURARINE.** (J. Lakowski, Rép. Chim. app. iii. 77.)—An alkaloïd obtained, together with oleandrine, from the leaves and branches of the oleander. (*Nerum Oleander*). By exactly precipitating the concentrated aqueous decoction with tannic acid, washing the precipitate with a little cold water, and then treating it with aqueous tannic acid for a short time only, tannate of pseudo-curarine is obtained in solution, while tannate of oleandrine remains behind.

The solution of the former is boiled with finely pulverised litharge, the filtrate evaporated nearly to dryness, the residue freed from oleandrine by ether, and the portion insoluble in that liquid is dissolved by alcohol.

On evaporating the alcoholic solution, pseudo-curarine remains as a yellowish, tasteless, inodorous varnish, very soluble in water and in alcohol, insoluble in ether, and non-volatile. It neutralises strong acids, but does not form crystallisable salts. The solutions are precipitated by mercuric and platinic chlorides. Pseudo-curarine appears to have no action on the animal organism.

The tannate of oleandrine left undissolved as above is taken up by ether; and the solution is treated with quicklime, which precipitates tannic acid and chlorophyll. On leaving the filtrate to evaporate, oleandrine is obtained as a slightly yellowish resinous, very bitter substance, slightly soluble in water, easily soluble in alcohol and in ether. It appears to form uncrystallisable salts, the solutions of which are precipitated by the chlorides of gold and platinum. Oleandrine acts as a local irritant, producing violent sneezing, vomiting, purging, and intermittent tetanus, sometimes with fatal results. When injected into the jugular vein of a dog or a rabbit it quickly destroys life.

**PSEUDODIALLYL-ALCOHOL.** See SECONDARY ALCOHOLS.

**PSEUDO-ERYTHRIN.** An old name of ethylic orsellinate (p. 236).

**PSEUDOHEXYL-ALCOHOL** or *Diallylic Monohydrate*. See SECONDARY ALCOHOLS.

**PSEUDO-HEXYL-GLYCOL** or *Diallylic Dihydrate*. See SECONDARY ALCOHOLS.

**PSEUDOLEUCINE.** See LEUCINE (iii. 582).

**PSEUDOLIBETHENITE.** $Cu^3P^2O^8.CuH^2O^2.H^2O$. (See PHOSPHATES OF COPPER, p. 561.)

**PSEUDOMALACHITE.** Syn. with PHOSPHOCALCITE, $Cu^3P^2O^8.3CuH^2O^2$ (p. 561).

**PSEUDOMORPH.** A mineral having a definite form, belonging, not to the substance of which it actually consists, but to some other substance which has wholly or partly disappeared. Pseudomorphs have been classed under four principal heads:—

1. *Pseudomorphs by alteration:* those formed by a gradual change of composition in the species, as when augite is altered to steatite.
2. *By substitution:* those formed by the replacement of a mineral or other substance which has been removed, or is gradually undergoing removal; *e. g.* the petrification of wood.
3. By *incrustration:* those formed by the incrustration of a crystal, which may be subsequently dissolved away, *the cavity* often being subsequently filled by infiltration; *e.g.* the change of fluor-spar to quartz.
4. By *paramorphism:* those formed when a mineral passes from one dimorphous state to another; *e.g.* change of arragonite to calcspar. (See GEOLOGY, CHEMISTRY OF,

ii. 833–836; also Dana's *Mineralogy*, i. 222, where a table of pseudomorphs is given.)

**PSEUDOMORPHINE.** See MORPHINE (iii. 1051).

**PSEUDO-ORCIN.** Syn. with ERYTHROMANNITE (ii. 504).

**PSEUDO-PROPYLIC ALCOHOL.** See TRITYLIC ALCOHOLS.

**PSEUDOPHITE.** A serpentine-like mineral from the Zdjar mountain near Aloysthal in Moravia: of specific gravity = 2·75—2·77, and containing, according to Haner, 33·42 per cent. $SiO^2$, 15·42 $Al^2O^3$, 34·04 MgO, 2·58 FeO, and 12·68 water, whence the formula $3(2MgO.SiO^2)(Al^2O^3.SiO^2) + 5H^2O$. (Kenngott, Wien. Akad. Ber. xvi. 170.)

**PSEUDOPURPURIN.** See PURPURIN.

**PSEUDOQUARTZITE.** A rock occurring in the Val-de-Tignes (Tarentaise in Savoy), very compact, of greyish white colour, and consisting of slender laminæ interlaced and cemented together by a quartz-like substance. Specific gravity = 2·704. Contains 79·90 per cent. $SiO^2$, 15·63 $Al^2O^3$, 0·44 $Fe^2O^3$, trace of lime, 0·94 MgO, 2·72 $K^2O$ (with trace of soda), trace of chlorine, and 1·58 water. (A. Terreil, Compt. rend. liii. 120; Jahresb. 1861, p. 1082.)

**PSEUDOQUININE.** A peculiar base said to have been obtained by Mengarduque (Compt. rend. xxvii. 221) from a cinchona extract of unknown origin. It neutralised acids completely, decomposed ammonium-salts, was insoluble in ether and in water, but soluble in alcohol, from which it crystallised in irregular prisms. Its solution in chlorine-water assumed a reddish-yellow colour on addition of ammonia, whereas quinine similarly treated turns green. It was tasteless, and its sulphate, which crystallised in flat prisms, was scarcely bitter. The base gave by analysis 76·6 per cent. carbon, 8·15 hydrogen, and 10·3 nitrogen.

**PSEUDOSTEAROPTENES.** A term applied by Klotzsch (J. pr. Chem. lv. 242) to the solid crystalline bodies separated by reduction of temperature from certain volatile oils and resins, and distinguished from the true stearoptenes by their greater solubility in hot water; such are the alyxia-camphor from *Alyxia aromatica;* geranium-camphor from *Pelargonium odoratissimum*, coumarin, the camphor of *Anthoxanthum odoratum;* auricula or primrose camphor from *Primula Auricula*, and the camphors of several other species of the same genus. These pseudo-stearoptenes often separate on the outer surface of the plants, as in *Primula* and *Ceropteris*.

**PSEUDOSTEATITE.** A mineral externally resembling talc, filling a cleft of the serpentine of Bathgate (Linlithgowshire). It is brittle, unctuous to the touch, has an uneven fracture; hardness = 2·2, and specific gravity = 2·469. Two analyses, *a* by Thomson, *b* by Binney (Edinb. Phil. J. 1862, xvi. 55), gave:

| | $SiO^2$. | $Al^2O^3$. | CaO. | MgO. | FeO. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|
| *a.* | 41·89 | 22·05 | 2·42 | 6·16 | 6·62 | 20·22 | = | 99·36 |
| *b.* | 42·78 | 22·53 | 2·54 | 6·76 | 6·31 | 18·68 | = | 99·60 |

**PSEUDOSULPHOCYANOGEN.** Syn. with PERSULPHOCYANOGEN (p. 380).

**PSEUDOTALCITE.** A mineral from the Val d'Arbonne (Tarentaise in Savoy), appearing under the microscope to consist of greenish, transparent, crystalline laminæ and small-pyramidal quartz-crystals. Before the blowpipe it loses its greenish colour, and in small pieces melts easily to a stony-vitreous whitish mass. According to Terrsil (Compt. rend. liii. 120) it contains 85·96 per cent. silica, 8·50 alumina, 1·40 ferric oxide, 0·77 lime, 1·31 magnesia, and 2·66 potash, with a trace of soda (= 100·60).

**PSEUDOTOXINE.** The name applied by Brandes to a light yellow poisonous extract prepared from belladonna leaves; soluble in water and aqueous alcohol, insoluble in ether and in absolute alcohol, precipitated by tincture of galls and acetate of lead, coloured green by iron-salts. It is not a pure substance, and owes its poisonous action to the presence of atropine. (Handw. vi. 683.)

**PSEUDO-URIC ACID,** $C^5H^6N^4O^4$. (Schlieper and Bayer, Instit. 1860, p. 182; Jahresb. 1860, p. 327.)—An acid obtained by the action of potassium-cyanate on dialuramide (uramil). Its potassium-salt is deposited in the crystalline form when dialuramide (or murexide) is heated with excess of potassium-cyanate till the liquid no longer turns red on exposure to the air; and on mixing the solution of the recrystallised salt in potash-ley with hydrochloric acid, the pseudo-uric acid is precipitated as a white crystalline powder made up of small prisms. It does not lose weight at 100°, is tasteless and inodorous, very slightly soluble in water, but easily soluble in caustic alkalis. It decomposes carbonates and acetates, and readily yields alloxan when treated with nitric acid. When suspended in water and heated with peroxide of lead, it gives off carbonic anhydride, and yields oxalate and pseudo-urate of lead, but no allantoïn; the mother-liquors probably contain oxalurate of lead as well as urea.

The pseudo-urates are easily obtained by the action of the acid on the corresponding hydrates, carbonates, or acetates; or they may be produced directly by the action of dialuramide on the corresponding cyanates.

The *ammonium-salt*, $C^5H^5(NH^4)N^4O^4.H^2O$, crystallises from the solution of the acid in hot dilute ammonia, in small laminæ or bulky needles, which are not more soluble in strong than in dilute ammonia, and do not take up an additional quantity of ammonia. It does not give up its crystallisation-water till heated above 100°; at 130° it turns red and gives off ammonia.—The *ethylamine-* and *aniline-salts* resemble the ammonium-salt.—The *potassium-salt*, $C^5H^5KN^4O^4.H^2O$, forms small shining scales which do not give up their water till heated above 140°, and decompose and turn red at 180°.—The *sodium-salt*, $C^5H^5NaN^4O^4.2H^2O$, forms cauliflower-like groups of prisms easily soluble in hot water, and giving off their water of crystallisation at 140°. From its solution in caustic soda it separates in the amorphous state, but without change of composition.

The *barium-salt*, $C^{10}H^{10}Ba''N^8O^8.5H^2O$, forms spherical groups of long slender needles.—The *calcium-salt* is obtained in fine prisms on precipitating the solution of either of the alkali-metal salts with chloride of calcium.

The *cupric*, *mercurous*, *mercuric*, and *lead-salts* are also crystallisable, the last with 1 at. water; the *silver-salt* is very easily decomposible.

**PSEUDOVERATRINE.** $C^{14}H^{20}N^2O^3$?—A resinous substance obtained from sabadilla-seeds: also called *Veratrin-resin*, and *Helonine* (from *Helonias officinalis*, the plant supposed to yield these seeds). It is prepared by treating the alcoholic extract of the seeds with water containing sulphuric acid, adding nitric acid by drops to the acid liquid, decanting the solution from the pitchy substance thereby separated, and precipitating with potash. The resulting precipitate is dissolved in alcohol, and the yellow resinous mass which remains on evaporating off the alcohol, is treated with water to extract sabadilline, and with ether to extract veratrine. Pseudoveratrine then remains behind. It is a brown substance, solid at ordinary temperatures, melting at 185°, and decomposing at a higher temperature, with evolution of nitrogenous products. It is soluble in alcohol, insoluble in water and in ether. It dissolves in acids, but does not neutralise them. (Couerbe, Ann. Ch. Phys. [2] lii. 352.)

**PSILOMELANE.** See Manganese, Oxides of (iii. 812).

**PSORALEA.** The undried root of *Psoralea esculenta* contains 0·63 nitrogen and 1·67 ash (Payen, Jahresb. 1849, p. 708).—*Psoralea glandulosa* or *Ilex paraguayensis* is the plant whose dried leaves yield Paraguay-tea (p. 349). According to Lenoble (J. Pharm. [3] xviii. 199), this substance contains a peculiar crystallisable nitrogenous body which he calls *psoralline;* but it is doubtless identical with *caffeine*, which has been shown by Stenhouse to exist in the dried leaves to the amount of 1·1 to 1·2 per cent.

**PTELEYL.** $C^3H^3$.—A radicle supposed by Kane to exist in the mesitylene-compounds: thus, trichloromesitylene $C^9H^9Cl^3$ was regarded as chloride of pteleyl, $C^3H^3Cl$.

**PTERITANNIC ACID.** $C^{21}H^{20}O^8$? (Luck, Jahrb. pr. Pharm. xxii. 173; Gm. xv. 500.)—An acid contained, together with tannaspidic acid, in the root of *Aspidium Filix mas.* When the coarsely pounded root is boiled with alcohol of 75 to 80 per cent. and the decoction is mixed with water, a small quantity of hydrochloric acid, and pulverised sulphate of sodium, a precipitate is formed containing the two acids. This precipitate is collected, washed with solution of sodic sulphate, pressed, again triturated with water, and digested for half an hour at 60°—80°, with water containing hydrochloric acid, whereby ammonia and other bases are removed. The residue washed with water, dried, and exhausted with ether free from alcohol, yields a solution of pteritannic acid and a residue of tannaspidic acid. The ethereal solution leaves on evaporation a black-brown residue, which is digested with distilled mineral naphtha as long as the oil is thereby coloured brown. The undissolved powder is collected, pressed, triturated and boiled with water, the resinous cake is dissolved in ether, and the solution is evaporated.

Pteritannic acid thus obtained is a black-brown, amorphous, shining mass, yielding a fawn-coloured electric powder. It is tasteless, but has a faint odour and slight acid reaction; insoluble in water, but soluble in alcohol and ether. The alcoholic solution forms brown precipitates with the chlorides of barium and calcium, and green precipitates with ferrous and ferric salts. With basic acetate of lead or with excess of the neutral acetate, it forms a precipitate containing $C^{21}H^{18}Pb''O^8$, and the liquid filtered therefrom yields with ammonia a precipitate containing $2C^{24}H^{28}Pb''O^8.Pb''H^2O^2$; by precipitation with a smaller quantity of the neutral acetate, an acid salt is formed containing $C^{24}H^{28}Pb''O^8.C^{24}H^{30}O^8$?

*Tetrachloropteritannic acid*, $C^{24}H^{26}Cl^4O^8$, is a light loam-coloured powder obtained by passing chlorine into water containing pteritannic acid in solution. It reacts with metallic salts like the latter. The alcoholic solution yields with basic acetate of lead a salt containing $C^{24}H^{24}Pb''Cl^4O^8.H^2O$.—*Hexchloropteritannic acid*, $C^{24}H^{24}Cl^6O^8$, is obtained, as an orange-coloured powder, by the action of dry chlorine on pteritannic acid. Its alcoholic solution yields with basic acetate of lead a precipitate containing $C^{24}H^{22}Pb''Cl^6O^8.H^2O$.

So-called *Ethylpteritannic acid.* When a solution of pteritannic acid in absolute alcohol is boiled with a small quantity of hydrochloric acid, a purple-red solution is formed which, when mixed with a small quantity of water, deposits a black-red resin containing $C^{52}H^{66}O^{15}$, and when dropt, with agitation, into a large quantity of water yields a light purple powder having the composition $C^{52}H^{68}O^{16}$. Luck regards these products as containing respectively $C^{52}H^{33}O^{15} = 2C^{24}H^{14}O^7.C^4H^5O$ and $C^{52}H^{34}O^{16} = 2C^{24}H^{14}O^7.C^4H^5O.HO$; but neither of them has actually been resolved into pteritannic acid and alcohol.

**PTYALIN.** A sulphuretted albuminous substance contained in the saliva of the parotid gland; it differs in some of its reactions from albumin, mucin, and casein. (Covecs, J. Pharm. [3] xlii. 92.)

**PTYCHOTIS AJOWAN.** An umbelliferous plant growing abundantly in Rajpootanah and other parts of Central India, and well known for its aromatic and carminative properties. The seeds, which resemble those of the caraway, excepting that they are much smaller, have a very agreeable odour, like that of thyme-oil, and when repeatedly distilled with water, yield an essential oil amounting to 5 or 6 per cent. of their weight and consisting of a hydrocarbon isomeric with oil of turpentine, holding in solution a camphor or stearoptene identical with thymol $C^{10}H^{14}O$ (*q. v.*). The hydrocarbon separated by fractional distillation and purified by treatment with chloride of calcium, potash, and potassium, is a colourless aromatic oil boiling at 172°, and having a density of 0·854 at 12°. When treated with hydrochloric acid, it yields, not a crystalline compound, but a brown mobile liquid. (Stenhouse, Ann. Ch. Pharm. xciii. 269; xcviii. 307; Chem. Soc. Qu. J. ix. 234.—Haines, Chem. Soc. Qu. J. viii. 289.)

**PUCCINE.** A doubtful alkaloïd said to exist, together with sanguinarine and another alkaloïd, called porphyroxine, in the root of *Sanguinaria canadensis.* (G. D. Gibb, Pharm. J. Trans. [2] i. 454.)

**PUDDLING.** See Iron (iii. 347).

**PULSATILLA-CAMPHOR.** Syn. with Anemonin (i. 291).

**PUMICE.** See Obsidian (p. 169).

**PUNAHLITE.** Syn. with Poonahlite (p. 688).

**PUNICA.** The root-bark of the pomegranate (*Punica Granatum*) yields when air-dried, 13·22 per cent., and when dried at 100°, 15·02 per cent. ash, containing 4·75 $K^2O$ (with trace of soda), 48·87 CaO, 1·84 MgO, 0·76 $Fe^2O^3$, 2·12 $P^2O^5$, 3·29 $SiO^2$, 0·98 $SO^3$, 0·46 Cl and 38·75 $CO^2$. (Spiess, Jahresb. 1860, p. 550.)

**PUNICIN.** An acrid uncrystallisable substance obtained from the bark of the pomegranate tree. (Righini, J. Pharm. [3] v. 298.)

**PURPLE, ANILINE.** See Aniline-dyes under Phenylamine (p. 466).

**PURPLE OF CASSIUS.** See Gold-purple (ii. 938).

**PURPLE COPPER.** *Variegated Copper. Erubescite.* A native sulphide of copper and iron (ii. 78).

**PURPLE CRUORIN.** A term applied by Stokes (Proc. Roy. Soc. xiii. 357) to the colouring matter (cruorin) of the blood when partially deoxidised; in its more highly oxidised state, it is called *scarlet cruorin.*

**PURPURATES.** Scheele, in 1776, observed that the solution of uric acid in nitric acid reddened the skin and left a deep-red residue when evaporated. Prout, in 1818, obtained this colouring matter in the crystalline form, and regarded it as the ammonium-salt of a peculiar acid, *purpuric acid;* by double decomposition he succeeded in obtaining other metallic purpurates, which were similarly coloured. He regarded the colourless substance which is separated from purpurate of ammonium by strong acids (murexan) as purpuric acid. Liebig and Wöhler (Ann. Ch. Pharm.

xxvi. 319), showed that Prout's purpuric acid did not possess the property of forming coloured salts, and so could not be considered as the acid of the purpurates; further, they regarded Prout's compound, not as an ammonium-salt but as an amide, and proposed to designate it murexide. Later researches, however, by Fritzsche (J. pr. Chem. xvi. 380; xvii. 42), and Beilstein (Ann. Ch. Pharm. cvii. 176), tend to establish it as a true ammonium-salt.

Purpuric acid has never been isolated, being decomposed when its salts are treated with a stronger acid. Taking the formula of the ammonium-salt as $C^8H^8N^6O^6 = C^8H^4(NH^4)N^5O^6$, the acid is represented by the formula $C^8H^5N^5O^6$. Laurent (Compt. rend. xxxv. 629) regards it as murexanic acid, the amic acid of alloxantin or murexic acid. Beilstein considers it as a dibasic acid, and regards murexide and other normal purpurates as acid salts.

Purpurates are all distinguished by their splendid purple colour; many are gold-green by reflected light.

*Purpurate of Ammonium* or *Murexide.*—This salt is formed in a great variety of circumstances:—1. By heating dialurate of ammonium: $2C^4H^5N^3O^3 + O = C^8H^8N^6O^6 + H^2O$ (ii. 315).—2. By the oxidation of dialuramide by the oxides of silver or mercury.—3. By exposing to the air, or adding alloxan to, an ammoniacal solution of dialuramide: $C^8H^4N^4O^7 + 2NH^3 = C^8H^8N^6O^6 + H^2O$.—4. By the action of ammonia on alloxantin (i. 139).—5. By exposing to the air an ammoniacal solution of murexan. A solution of uric acid in dilute nitric acid, as it contains alloxan and alloxantin, yields purpurate of ammonium on addition of ammonia. It is by this process that murexide is prepared on the manufacturing scale for use in dyeing. According to Beilstein, the best method of preparing murexide is by the action of mercuric oxide on dialuramide. 4 pts. of dialuramide and 3 pts. of mercuric oxide are dissolved in 30 to 40 pts. of water, a little ammonia is added, and the whole is boiled for a few minutes, and filtered off; the filtrate on cooling deposits crystals of murexide, the quantity of which is increased by adding carbonate of ammonium when the liquid is nearly cool. Gregory prepares it by dissolving 4 pts. alloxantin and 7 pts. tetrahydrated alloxan in 240 pts. boiling water, and adding 80 pts. of a cold saturated solution of carbonate of ammonium. Fritzsche's method of adding carbonate of ammonium to a boiling solution of alloxan probably depends upon the formation of alloxantin by the action of heat on the alloxan-solution, since with pure alloxan no murexide is obtained. Gmelin obtains it by the long-continued action of dry ammonia on finely-pounded alloxantin, the resulting brown-red mass being repeatedly pulverised, and exposed anew to the action of the gas; the free ammonia is then removed, and the product dissolved in as little hot water as possible, and crystallised.

Purpurate of ammonium crystallises in four-sided prisms, which are garnet-coloured by transmitted, rich gold-green by reflected, light. They contain 1 at. (6·54 per cent.) water of crystallisation, which they lose when heated to 100°, or when dried in vacuo over sulphuric acid; they are then converted into a brown-red powder, which acquires under the burnisher a green colour and metallic lustre. It is slightly soluble in cold *water*, more easily in hot water, forming a splendid purple solution; insoluble in alcohol or ether. The aqueous solution of purpurate of ammonium is decomposed by *hydrochloric* or *sulphuric acid*, murexan being precipitated, while the supernatant liquid contains alloxan, alloxantin, urea, and ammonia. Purpurate of ammonium dissolves in cold *potash*, with evolution of ammonia, forming an indigo-blue solution, which is decolorised by heat, after which the addition of sulphuric acid precipitates murexan. Nitric acid converts murexide into alloxan. An aqueous solution of murexide is decomposed by *sulphuretted hydrogen*, murexan being precipitated, while the supernatant liquid contains alloxantin and dialuric acid; no hydrosulphate of ammonium is formed. Heated with *cyanate of potassium*, it yields pseudo-urate of potassium (p. 745).

Various formulæ have been proposed for purpurate of ammonium. Liebig and Wöhler give $C^6H^6N^5O^4$; Kodweiss, $C^3H^4N^4O^4$; Fritzsche, $C^8H^8N^6O^{5.5}$. That adopted by Gmelin, Gerhardt, Laurent, Beilstein, &c., and now generally accepted, is $C^8H^8N^6O^6$. The following are the results of analysis:

| | | Calc. | Kodweiss at 100°. | L. and W. | Liebig. | Fritzsche at 100°. | Beilstein at 160°. |
|---|---|---|---|---|---|---|---|
| $C^8$ | 96 | 33·80 | 38·96 | 34·08 | 34·4 | 34·93 | 34·18 |
| $H^8$ | 8 | 2·82 | 2·70 | 3·00 | 3·0 | 2·83 | 3·11 |
| $N^6$ | 84 | 29·58 | 36·34 | 32·90 | 31·8 | 30·80 | 30·35 |
| $O^6$ | 96 | 33·80 | 22·00 | 30·02 | 30·8 | 31·44 | 32·36 |
| $C^8H^8N^6O^6$ | 284 | 100·00 | 100·00 | 100·00 | 100·0 | 100·00 | 100·00 |

Murexide is used in dyeing for the production of various shades of red, purple, and yellow. Its solution mixed with mercuric salts produces fine red and purple colours on silk, wool, cotton, and leather; and with zinc-salts it yields orange and yellow colours. The colours thus obtained are very fresh and brilliant, and may be exposed to light without fading; they are however excessively sensitive to the action of sulphurous acid, which tarnishes and discolours them with extreme rapidity. This is a great drawback to their employment in places where the use of coal-gas has become general.

A few years ago, murexide was very largely used for dyeing and calico-printing, the weekly yield of one factory alone, that of Mr. Rumney of Manchester, having amounted to no less than 12 cwt.; but it has since been nearly driven out of the field by the aniline colours. (*Report on Murexide-dyeing by* E. Kopp, Rép. Chim. app. i. 79; also Hofmann's *Report*, 1862, p. 118.—Jahresb. 1857, p. 649; 1858, p. 671; 1860, p. 752.)

*Purpurate of Potassium*, $C_8H_4KN_5O_6$.—Obtained as a brown-red crystalline powder, when concentrated solutions of purpurate of ammonium and nitrate of potassium are mixed together; when freed from murexide by boiling with nitre, and recrystallised, it is obtained in crystals resembling those of the ammonium-salt, but darker. It is slightly soluble in water, still less in saline solutions. After drying at 100° it loses 3·04 per cent. water at 300° (Fritzsche); 2·95 per cent. (Beilstein). The deep blue colour of a solution of murexide in cold potash appears to be owing to the presence of a basic potassium-salt.

The *sodium-salt*, $C_8H_4NaN_5O_6$, is obtained like the potassium-salt.

The *barium-salt*, $C_{16}H_8Ba''N_{10}O_{12}$, is obtained by precipitating acetate of barium with murexide. It is a dark-green powder, which becomes purple-red when triturated; slightly soluble in water, forming a purple solution. At 100° it loses 8·78 per cent. water.

The *strontium-* and *calcium-salts* are similarly obtained with nitrate of strontium and chloride of calcium. They are slightly soluble with a purple colour.

The *magnesium-salt* is very soluble, with purple colour.

The *lead-salt* has not been obtained pure. Murexide added to an acid solution of acetate of lead gives a red solution which gradually deposits red crystals which are not homogeneous.

*Silver-salts.*—The *mono-argentic salt*, $C_8H_4AgN_5O_6$, is obtained when a rather dilute solution of murexide is added to a dilute solution of nitrate of silver acidulated with nitric acid. It forms crystals resembling those of the ammonium-salt; it gives off its water (5·71 per cent.) at 100°.

A *di argentic salt*, $C_8H_3Ag_2N_5O_6$, is obtained as a brown-red powder by precipitating a cold saturated solution of murexide with nitrate of silver. With ammoniacal nitrate of silver, murexide yields a deep violet precipitate containing $C_8H_3Ag_2N_5O_6.2Ag_2O$. (Beilstein.)

A solution of murexide is coloured yellow, but not precipitated, by trichloride of gold or tetrachloride of platinum. (Beilstein.) F. T. C.

**Isopurpurates.** $C_8H_4MN_5O_6$ (iii. 433).—These salts, produced by the action of cyanide of potassium (and other cyanides) on picric acid, have the same composition as the purpurates, and resemble them very closely in their properties; indeed isopurpurate of ammonium is undistinguishable from murexide, and according to E. Kopp may be used for dyeing in the same way as the latter.

**Metapurpurates,** $C_8H_5MN_4O_4$. (Pfandler and Oppenheim, Bull. Soc. Chim. 1865, ii. 99.)—The *potassium-salt*, $C_8H_5KN_4O_4$, is produced by the action of cyanide of potassium on dinitrophenic acid, and differs from the purpurate or isopurpurate, $C_8H_4KN_5O_6$, in the same manner as dinitrophenic acid differs from trinitrophenic (picric) acid, that is to say, by containing 1 at. hydrogen more, and 1 at. nitryl less. It is prepared by dropping a solution of potassium-cyanide heated to 60° into an aqueous or alcoholic solution of dinitrophenic acid, and separates on cooling in the form of a very dark-coloured crystalline powder. It may be purified by washing with a small quantity of cold water, recrystallisation from warm water, then pressing it in a cloth and drying over oil of vitriol. When moist or in solution, it is very unstable, being decomposed at the temperature of the water-bath, but if once dried in the air, it may be heated to 100° without decomposition; at that temperature it retains 1 at. water of crystallisation, which it gives off (7·31 per cent.) at 150°.

The solution of this potassium-salt gives dark-brown precipitates with most metallic solutions and with the chlorides of barium and strontium. The *silver-salt*, $C_8H_5AgN_4O_4$ which is red and has a green metallic lustre, obstinately retains a portion of the potassium-salt used in its preparation.

**PURPUREÏN** or **PURPURAMIDE.** (Stenhouse, Proc. Roy. Soc. (1863)

xii. 633; xiii. 145.—Schützenberger and Schiffert, Bull. Soc. industr. de Mulhouse, 1864, p. 70; Jahresb. 1864, p. 543.)—A product formed by the action of ammonia on purpurin. A recently prepared solution of purpurin in ammonia deposits purpurin unaltered on addition of hydrochloric acid; but if left to itself for a day or heated to 100°, it yields, on addition of hydrochloric or dilute sulphuric acid, a dark violet-coloured precipitate, which dissolves in alcohol with deep violet colour, and separates therefrom in crystals resembling murexide (Schützenberg and Schiffert); in dark crimson microscopic needles, exhibiting a fine iridescent green colour by reflected light. (Stenhouse.)

Stenhouse designates this substance as purpureïn (from its analogy to orceïn), and represents it provisionally by the formula $C^{32}H^{24}N^2O^{10}$; Schützenberger and Schiffert regard it as purpuramide, and as formed from purpurin (to which they assign the formula $C^{20}H^{12}O^7$), according to the equation, $C^{20}H^{12}O^7 + NH^3 - H^2O = C^{20}H^{13}NO^6$.

According to Stenhouse.

| | | Calc. | Found. |
|---|---|---|---|
| $C^{32}$ | 396 | 65·13 | 65·29 |
| $H^{24}$ | 24 | 3·95 | 4·01 |
| $N^2$ | 28 | 4·60 | 4·60 |
| $O^{10}$ | 160 | 26·32 | 26·10 |
| | 608 | 100·00 | 100·00 |

According to Schützenberger and Schiffert.

| | | Calc. | Found. |
|---|---|---|---|
| $C^{20}$ | 240 | 66·11 | 66·47 |
| $H^{13}$ | 13 | 3·58 | 4·14 |
| N | 14 | 3·85 | 4·19 |
| $O^6$ | 96 | 26·46 | 26·20 |
| | 363 | 100·00 | 100·00 |

The analytical results leave no doubt as to the identity of the two products. The formula proposed by Schützenberger and Schiffert is perhaps the more probable of the two (provided their formula of purpurin is correct), though it does not agree quite so closely with the analysis as the other, and moreover the compound has not been shown to possess the characters of an amide. Stenhouse regards the formation of his purpureïn as analogous to that of orceïn from orcin (p. 211), that is to say as depending on the joint action of ammonia and oxygen (he exposed a solution of purpurin in dilute ammonia to the air for about a month, renewing the water and ammonia as they evaporated); but according to Schützenberger and Schiffert, the formation of the ammoniacal compound of purpurin does not depend on oxidation, the same product being obtained, and more quickly, when the ammoniacal solution is heated to 100° in a closed vessel. It must be observed also that Stenhouse's purpureïn was obtained from purpurin prepared from madder by E. Kopp's process (iii. 749), which, according to Schützenberger and Schiffert, is not a definite product (see Purpurin).

Purpureïn or purpuramide is nearly insoluble in sulphide of carbon and in cold dilute acids, slightly soluble in ether and in cold water, more easily in hot water, very easily in alcohol and in dilute aqueous alkalis. From its solution in cold concentrated sulphuric acid, it is precipitated by water in its original state. Its solution in ether or in alcohol containing acetic acid exhibits, according to Stokes, absorption-bands resembling those of purpurin in character, but differing in situation.

The aqueous solution of purpureïn is precipitated, like that of orceïn, by *chloride of sodium*. It forms a red precipitate with *chloride of zinc*, purple gelatinous with *mercuric chloride*, dark brown with *nitrate of silver*. It dyes silk and wool a fine rose-red or amaranth-red without the aid of mordants, but mordanted vegetable fabrics are not permanently coloured by it.

The solution of purpureïn in aqueous alcohol gives with *bromine-water*, a yellow amorphous precipitate, and the evaporated filtrate deposits on cooling a small quantity of a brown resinous powder. A solution of purpureïn in *nitric acid* of specific gravity 1·35, deposits on cooling, scarlet prisms of nitropurpureïn, insoluble in water, ether and sulphide of carbon, nearly insoluble in alcohol, but soluble in hot nitric acid. (Stenhouse.)

**PURPUREOCOBALTIC SALTS.** See Cobalt-bases, Ammoniacal (i. 1052).

**PURPURIC ACID.** See Purpurates (p. 747).

**PURPURIN.** $C^9H^6O^3$ according to Debus and Stenhouse; $C^{20}H^{12}O^7$ according to Schützenberger. *Oxylizaric acid* of Debus; *Madder-purple* of Runge; *Matière colorante rose* of Gaulthier de Claubry. (Colin and Robiquet, Ann. Ch. Phys. [2] xxxiv. 244. Gaulthier de Claubry and J. Persoz, *ibid.* xlviii. 69.—Persoz, *ibid.* li. 110.—Runge, *ibid.* lxiii. 282.—J. Schiel, Ann. Ch. Pharm. lx. 74; Debus, *ibid.* lxvi. 351; lxxxvi. 117.—Wolff and Strecker, *ibid.* lxxv. 1.—Rochleder, *ibid.* lxxx. 321; lxxxii. 205.—Stenhouse, Proc. Roy. Soc. xii. 633; xiii. 145.—Schützenberger and Schiffert, Bull. Soc. industr. de Mulhouse, 1864, p. 70; Jahresb. 1864, p. 542.—Schützenberger, Bull. Soc. Chim. 1865, ii. 12.)—A red colouring matter extracted from madder by the same processes as alizarin (i. 113; iii. 742), and separated therefrom by its greater solubility in alum-liquor. Debus prepares it by adding dilute sulphuric acid to the alum-solutions from which the alizarin has separated by cooling, and boils the precipitate which forms after 12 or 14 hours, with dilute hydrochloric acid, to free it from alumina. It is then washed with water and recrystallised from alcohol. For other processes, see *Gmelin's Handbook* (xiii. 326).

E. Kopp extracts purpurin from madder by macerating the ground root in dilute aqueous sulphurous acid, mixing the filtrate with sulphuric acid, and heating the liquid to 30° or 40° (iii. 749). But according to Schützenberger and Schiffert, the red or orange-coloured flakes thus precipitated are not a definite compound, but may be separated, by the successive use of alcohol and benzene, into purpurin or oxyalizarin, $C^{20}H^{12}O^{7}$, pseudopurpurin or trioxyalizarin, $C^{20}H^{12}O^{8}$, an orange-red colouring matter, consisting of hydrate of purpurin, $C^{20}H^{16}O^{9}$, and a yellow colouring matter, $C^{20}H^{12}O^{6}$, isomeric or polymeric with alizarin (p. 751).

Stenhouse's method of extracting purpurin from East Indian madder, or munjeet, is described under MUNJISTIN (iii. 1061).

Purpurin exhibits some diversity of physical properties according to the circumstances of its preparation. From strong alcohol it crystallises in red needles; from weak alcohol in soft slender orange-coloured needles containing 4·8 per cent. water, ($C^{9}H^{6}O^{3}.\frac{1}{2}H^{2}O$), which they give off at 100°, assuming a red colour (**Wolff** and **Strecker**). According to Schützenberger and Schiffert, the anhydrous compound crystallises from hot alcohol, the hydrate from cold alcohol (p. 751). The anhydrous compound melts when heated, and sublimes with partial decomposition, leaving a carbonaceous residue. Respecting the optical characters of its solutions, see LIGHT (iii. 638, footnote).

The composition of anhydrous purpurin is variously stated by Debus and by Stenhouse on the one hand, by Schützenberger and Schiffert on the other.

| | | | Debus, mean. | Stenhouse. | | | | Schütz. & Schiff. mean. |
|---|---|---|---|---|---|---|---|---|
| $C^{9}$ | 108 | 66·67 | 66·40 | 66·46 | $C^{20}$ | 240 | 65·93 | 65·83 |
| $H^{6}$ | 6 | 3·70 | 3·86 | 3·55 | $H^{12}$ | 12 | 3·29 | 3·37 |
| $O^{3}$ | 48 | 29·63 | 29·74 | 29·99 | $O^{7}$ | 112 | 30·78 | 30·80 |
| $C^{9}H^{6}O^{3}$ | 162 | 100·00 | 100·00 | 100·00 | $C^{20}H^{12}O^{7}$ | 364 | 100·00 | 100·00 |

The purpurin analysed by Debus was obtained from ordinary madder by the process above described; that of Stenhouse from munjeet; that of Schützenberger and Schiffert from the crude purpurin prepared by E. Kopp's process, by extraction with hot alcohol. The formula they assign to it represents it as oxyalizarin, alizarin being regarded as $C^{20}H^{8}O^{6}$.

Purpurin is more soluble in *water* than alizarin, and forms a reddish solution. It dissolves also in *alcohol* and in *ether;* the alcoholic solution is redder than that of alizarin. It is easily soluble in a boiling solution of *alum*, forming a liquid of a beautiful pink colour with yellow fluorescence, and remains dissolved after cooling, whereas alizarin is deposited from the same solution on cooling. *Oil of vitriol* and *fuming sulphuric acid* also dissolve purpurin, the latter decomposing it when heated to 200°. It is less easily attacked than alizarin by *nitric acid;* on boiling the liquid, phthalic and oxalic acids are formed. Purpurin dissolves in caustic *alkalis*, and at the boiling heat in *sodic carbonate*, with cherry-red or bright red colour, whereas alizarin forms blue solutions. The alkaline solutions of purpurin decompose on exposure to the air, the colour of the liquid changing from bright red to reddish-yellow, and ultimately disappearing almost entirely, after which purpurin can no longer be detected in the liquid: alizarin, on the other hand, suffers no such decomposition (**Schunck**). These characters, together with the peculiar spectrum formed by its solutions, sufficiently distinguish purpurin from alizarin.

Purpurin dissolves in *ammonia*, and the solution, after exposure to the air, or after being heated to 100° in a close vessel, deposits purpureïn, on addition of acids (p. 749).

An alcoholic solution of purpurin forms with *acetate of lead* a purple precipitate containing 46·6 per cent. lead-oxide, agreeing approximately with the formula $5C^{18}H^{10}Pb''O^{6}.Pb''O$, which requires 46·7 per cent. (**Wolff** and **Strecker. Debus.**)

Compounds of purpurin with *potash* and *soda* are obtained as nearly black crystalline precipitates, on mixing the alcoholic solutions of purpurin and the alkalis. On heating these compounds to 150° with ethylic iodide and alcohol, red crystalline grains are obtained, slightly soluble in alcohol and consisting of **ethylpurpurin** $C^{22}H^{16}O^{7} = C^{20}H^{11}(C^{2}H^{5})O^{7}$ (analysis 66·82 per cent. C and 4·51 H; calc. 67·34 C and 4·08 H). (**Schützenberger** and **Schiffert.**)

*Compounds obtained from Emile Kopp's* "purpurin" *by the action of solvents* (Schützenberger and Schiffert). This crude purpurin is partially soluble in cold alcohol. The insoluble portion contains: α. Purpurin or oxyalizarin $C^{20}H^{12}O^7$, which dissolves in boiling alcohol; and β. Pseudopurpurin or trioxyalizarin $C^{20}H^{12}O^9$, which is insoluble in boiling alcohol, but dissolves in hot benzene and crystallises therefrom in slender brick-red needles. The cold alcoholic extract contains: γ. An orange-red colouring matter, consisting of hydrate of purpurin $C^{20}H^{16}O^9 = C^{20}H^{12}O^7.2H^2O$; and δ. A yellow colouring matter, isomeric with alizarin $C^{20}H^{12}O^6$. The latter is soluble in benzene; the former is insoluble in that liquid, but dissolves very easily in alcohol, and separates therefrom, sometimes as a curdy mass, sometimes in orange-red laminæ.

The centesimal composition of the three last-mentioned products, as determined by analysis, is as follows:

| | *Pseudopurpurin.* | | | *Hydrate of Purpurin.* | | | *Yellow Colouring matter.* | |
|---|---|---|---|---|---|---|---|---|
| | Calc. | Mean of Anal. | | Calc. | Mean of Anal. | | Calc. | Anal. |
| $C^{20}$ | 60·60 | 61·05 | $C^{20}$ | 60 | 59·93 | $C^{20}$ | 68·96 | 67·90 |
| $H^{12}$ | 3·03 | 2·97 | $H^{16}$ | 4 | 4·13 | $H^{12}$ | 3·44 | 3·55 |
| $O^9$ | 36·37 | 35·98 | $O^9$ | 36 | 35·94 | $O^6$ | 27·60 | 28·55 |
| | 100·00 | 100·00 | | 100 | 100·00 | | 100·00 | 100·00 |

Pseudopurpurin and hydrate of purpurin are converted into purpurin by sublimation (leaving a considerable residue of charcoal) or by heating with alcohol to 180°—200°.

The yellow colouring matter sublimes almost without decomposition. It may be produced from purpurin, pseudopurpurin or hydrate of purpurin, by heating to 180° with water and iodide of phosphorus, or more easily by the action of stannous chloride on a boiling alkaline solution.

Purpurin, pseudopurpurin, and hydrate of purpurin impart to mordants colours resembling those of alizarin; the tint communicated by them to alumina-mordants is more reddish, and without blue reflex. The colours produced on tissues by purpurin and its hydrate resist the action of boiling soap-water tolerably well, whereas those formed by pseudopurpurin are completely destroyed thereby. The resistance is therefore nearly in inverse proportion to the amount of oxygen in the colouring matter. The yellow colouring matter produces with alumina-mordant a rather dull yellow, which is destroyed by soaping and by immersion in a bath of stannic chloride. (Schützenberger.)

**PURPURINO.** Syn. with Porporino (p. 691).

**PURREE.** A yellow colouring matter imported into Europe from India and China in round lumps weighing three or four ounces, brown on the outside, of a deep orange-yellow colour within, and exhibiting, according to Erdmann, a crystalline structure. Respecting its origin, various and contradictory statements have been made. According to most authorities it is of animal origin, and is deposited from the urine of camels, elephants, and buffalos, especially after the animals have eaten certain plants (the fruit of *Mangostana mangifer* for example); according to others, it is an intestinal or biliary concretion of the same animals: Stenhouse, on the other hand, supposes it to be a vegetable substance prepared by evaporating down a vegetable juice mixed with magnesia. Its peculiar odour resembling that of castoreum is, however, in favour of the former supposition.

Purree serves for the preparation of Indian yellow, a fine rich durable yellow colour much used both in oil and water-colour painting, and consisting mainly of euxanthate of magnesium (see Euxanthic Acid, ii. 609); according to Wagner, it also contains alumina. Indian-yellow being somewhat costly is often adulterated with cheaper yellow pigments, chrome-yellow for example. According to M. Haro, jun., a colour maker in Paris, pure Indian yellow burns like amadou, leaving a comparatively small residue, whereas the adulterated article burns more slowly, and leaves a larger residue. (*Chimie des Couleurs*, par J. Lefort, Paris, 1855.)

**PURREIC ACID.** Syn. with Euxanthic Acid.

**PURRENONE.** Syn. with Euxanthone.

**PUS.** A pathological product, the result of certain diseased actions of the animal body. Typical pus, "laudable" pus, is a thick yellowish liquid of the consistency and appearance of cream, but its physical and chemical characters vary exceedingly according to the kind of tissue from which it comes and the nature of the disease giving rise to it. Its reaction is generally alkaline, but sometimes neutral or acid. It consists of pus-corpuscles floating in a pus-serum; the separation of the two by filtration, though tedious, is practicable.

The protein-constituents of pus have been as yet but imperfectly studied. The serum contains an albumin apparently identical with that of blood-serum, together with globulin or myosin. From the corpuscles also may be obtained a substance possessing some but not all of the reactions of myosin (Hoppe-Seyler, Phys. Chem. Analyse, p. 363). In many but not all specimens of pus may be found the so-called pyin, which has the following reactions. It is precipitated from its solutions by acetic acid, the precipitate being insoluble in excess of the reagent. Nitric and hydrochloric acids give precipitates readily soluble in excess. Ferrocyanide of potassium produces no precipitate in the hydrochloric acid solution. A solution of pyin is unaltered by boiling. Pyin closely resembles mucin (said to be found in pus from mucous membranes), differing from it, however, in being precipitated by mercuric chloride and neutral acetate of lead. Gelatin and chondrin have been found at times in pus.

Among the fatty bodies always present in pus may be mentioned cholesterin, olein, palmitin (the last two also in combination with alkalis), cerebric and glycero-phosphoric acid. According to Fischer (Med. Cblt. 1865, p. 225), the only fatty body besides cholesterin in good fresh pus is protagon, whose speedy decomposition gives rise to the rest. The same observer also states that butyric, formic and valerianic acids when present are putrefactive products. Bödeker found in specimens of pus, a substance called by him *chlorrodinic acid.*

Sugar and urea have occasionally been found; and leucine may be regarded as a constant constituent unless it be a product of putrefaction (Fischer). Pus from wounds often has a blue colour, very distinctly seen when dried on bandages, &c.; this arises from the presence of Pyocyanin, which may be isolated in the following way. The bandages, &c. are steeped in water containing a few drops of ammonia, and the resulting green liquid is filtered, partially evaporated, and again filtered. The filtrate is shaken with chloroform, which takes up the colouring matter; and the chloroform solution is treated with very dilute sulphuric acid until it turns quite red. On standing a red aqueous layer separates which is removed, treated with caustic baryta until it changes to blue, filtered, and the filtrate again shaken with chloroform. The blue chloroform solution is allowed to evaporate in the air. Pyocyanin crystallises in needles or in rectangular flakes. It is soluble in chloroform, alcohol, and water, with difficulty in ether. Acids turn it red; alkalis restore the blue colour. Chlorine destroys it. After the separation of the pyocyanin, the chloroform retains in solution a yellow substance called pyoxanthose, which remains on leaving the solution, previously freed from fat, to evaporate spontaneously. It is sometimes, though rarely, obtained in groups of microscopic needles. It is very slightly soluble in water, more soluble in alcohol, ether, chloroform, and benzene. Acids turn it red, alkalis violet (Fordos, Compt. rend. lvi. 1128; Jahresb. 1863, p. 657). W. B. Herapath finds indigo-blue in blue pus (Brit. Assoc. Trans. 1864, p. 124).

The ashes of pus consist mainly of chloride of sodium, with alkaline and earthy phosphates, alkaline carbonates, sulphate of calcium, and oxide of iron.

The quantitative analyses of pus, as might be expected, differ widely. The following (Bibra) may be taken as an average. In 1,000 parts: water 862, solids 138, whereof albumin 91, fats and cholesterin 12, extractives 29, salts 9.

Masse (Simon's Chem. Syd. Soc. trans. ii. 692) thus compares 1,000 parts

| | Pus-serum. | Blood-serum. |
|---|---|---|
| Water . . . . . | 890·00 | 906·5 |
| Solid residue . . . | 110·00 | 93·5 |
| Organic constituents . . | 92·58 | 85·7 |
| Chloride of sodium . . | 12·60 | 4·6 |
| Carbonate of sodium . . | 2·22 | 1·4 |
| Phosphate of sodium . . | ·32 | ·9 |
| Sulphate of sodium . . | ·18 | ·2 |
| Phosphate of calcium . . | 1·20 | 0·7 |
| Carbonate of calcium . . | ·90 | |

M. F.

**PUSCHKINITE.** A variety of lime and iron epidote from the Western Ural, north of Katherinenburg. (See Epidote, ii. 490.)

**PUTRANGIRA.** *Putrangira Roxburghii*, an East Indian plant, yields a fat oil melting at +31°. (Lepine, J. Pharm. [3] xl. 16.)

**PUTREFACTION.** See Fermentation (ii. 623); also *Ure's Dictionary of Arts, &c.* (iii. 548).

**PYCNITE.** A massive subcolumnar variety of topaz (*q. v.*).

**PYCNOMETER.** An instrument for determining the specific gravities of aerated mineral waters. (Fresenius, Zeitschr. Anal. Chem. i. 178.)

**PYCNOTROPE.** See SERPENTINE.

**PYIN.** See PUS.

**PYOCYANIN.**
**PYOXANTHOSE.** } See PUS (p. 752).

**PYRACONITIC ACID.** Syn. with ITACONIC ACID.

**PYRALLOLITE.** The name of a series of decomposition-products of augite and occasionally of hornblende, consisting mainly of magnesian hydrosilicates. They blacken when heated, then burn white if in contact with the air, and give off water having an empyreumatic odour, due to the presence of organic matter. When very strongly heated before the blowpipe, they become rounded on the edges only. The pyrallolite of Storgård is converted by strong sulphuric acid, with incipient tumefaction and decomposition of the organic matter, first into a reddish, then into a black powder. The same decomposition appears to be produced also by dilute sulphuric acid, for the mineral after being treated with it, is no longer blackened by the strong acid.

Pyrallolites have been analysed by Nordenskiold (Schw. J. xxxi. 386), Arppe, Furuhjelm, Runeberg and Selin (Anal. af Finsk. Min. p. 35), and Bischof (*Lehrbuch d. Chem. Geolog.*, i. 516).

*a.* From Kullakalkbruch: Kimite. Green or blue-green; partly still exhibiting distinct augite structure. Specific gravity = 2·7. Hardness = 3—4 (Runeberg).—*b.* Takvedaholm, in calcspar. Green; fibrous. Specific gravity = 2·70. Hardness = 3—4 (Arppe).—*c.* Skrähböle, in quartz. Green, fibrous or granular. Specific gravity = 2·73. Hardness = 2—3 (Arppe).—*d.* Haapakylä; greenish, loosely granular aggregate in calcspar. Specific gravity = 2·61 (Arppe).—*e.* Kullakalkbruch; white, with augitic structure. Hardness = 3—4 (Arppe).—*f.* Storgård, Pargas (Nordenskiold.—*g.* Frugård; light-brown or yellow-grey columnar masses cleavable in one direction. Specific gravity = 2·66. Hardness = 3 (Arppe).—*h.* Kullakalkbruch; white, earthy (Selin).—*i.* From the same; greenish-white, earthy (Furuhjelm).

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* | *k.* |
|---|---|---|---|---|---|---|---|---|---|---|
| Silica | 48·88 | 55·17 | 55·92 | 57·49 | 56·9 | 56·62 | 63·87 | 58·87 | 66·18 | 76·23 |
| Alumina | 0·48 | 1·13 | 1·55 | 1·11 | 1·4 | 3·38 | 0·34 | 1·79 | 0·87 | 1·79 |
| Magnesia | 24·72 | 6·85 | 26·12 | 30·05 | 28·7 | 23·38 | 23·19 | 18·39 | 18·77 | 11·65 |
| Lime | 10·69 | 6·33 | 6·34 | 2·90 | 3·9 | 5·58 | 3·74 | 11·72 | 5·53 | 2·56 |
| Ferrous oxide | 1·55 | 21·45 | 1·86 | 1·26 | 0·6 | 0·89 | 2·18 | 0·57 | 1·83 | 0·72 |
| Manganous oxide | 5·76 | 0·09 | 1·68 | 0·69 | . . | 0·99 | | | | |
| Loss at 100° | . . | . . | . . | . . | . . | 3·58 | 7·35 | 8·78 | 6·48 | 3·05 |
| Loss on ignition | 12·33 | 9·15 | 7·56 | 7·30 | 8·5 | 5·48 | | | | 4·05 |
| | 99·41 | 100·17 | 101·03 | 100·80 | 100·0 | 99·90 | 100·64 | 100·12 | 99·66 | 100·05 |

These analyses appear to indicate a gradual transition from the composition $M^2O.SiO^2.H^2O$ to $M^2O.4SiO^2.H^2O$, the silica being partially also replaced by alumina.

**PYRANTIMONITE.** Syn. with Kermesite or Red Antimony (iii. 446).

**PYRARGILLITE.** A silicate occurring in the granite of Helsingfors, Finland, in prismatic forms with indistinct cleavage. Hardness = 3·5. Specific gravity = 2·5. It is partly black or bluish, liver-brown or dull red, with a dull resinous lustre; has an argillaceous odour. Infusible before the blowpipe, but becomes slightly glazed in a strong heat. Soluble in hydrochloric acid. Contains, according to Nordenskiold's analysis (Berz. Jahresb. 1833, p. 174):

| $SiO^2$. | $Al^2O^3$. | $Fe^2O^3$. | MgO. | $K^2O$. | $Na^2O$. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|
| 43·93 | 28·93 | 5·30 | 2·90 | 1·05 | 1·85 | 15·47 | = | 99·43 |

The mineral may be regarded as an altered dichroïte (ii. 320), containing $\frac{2}{3}$ of the strong bases of that mineral. (Bischof.)

**PYRARGYRITE.** *Dark-red silver ore. Ruby silver. Black silver. Aerosite. Argyrythrose. Dunkles Rothgültigerz. Antimonsilberblende. Argent antimonié sulfuré. Argentum rubrum.*—Native sulphantimonite of silver, occurring in rhombohedral crystals, in which, for the rhombohedron R, the principal axis = 0·7945, and the angle R : R in the terminal edges = 108° 20′. The crystals are chiefly prismatic, formed by the combination of $\infty P2$ with R and other rhombohedrons and scalenohedrons. (For figures, see Dana, ii. 77, 78.) Cleavage rather imperfect parallel to R. Twins are of frequent occurrence. The mineral is also found massive, with granular structure, sometimes impalpable. Hardness = 2—2·5. Specific gravity = 5·7—5·9. Translucent to opaque, with metallic adamantine lustre and black colour, sometimes approaching to cochineal-red. Streak, cochineal-red. Fracture, conchoïdal. Sectile, yielding readily to the knife. Before the blowpipe it melts and gives out fumes of antimony, and on charcoal ultimately leaves a globule of silver. Dissolves in hot nitric acid, leaving sulphur and antimonious oxide.

*Analyses:—a.* From Andreasberg in the Hartz (Bonsdorf, Schw. J. xxxiv. 235).—*b.* From Mexico (Wöhler, Ann. Ch. Pharm. xxvii. 157).—*c.* From the Mularoche mine near Zacatecas in Mexico. (Böttger, *Ramm. Mineralch.* p. 83.)

| | *Calculation.* | | *Analyses.* | | |
|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* |
| $S^3$ | 96 | 17·77 | 17·78 | 18·0 | 17·76 |
| Sb | 120 | 22·28 | 23·26 | 21·8 | 24·59 |
| $Ag^3$ | 324 | 59·95 | 58·96 | 60·2 | 57·45 |
| $Ag^3SbS^3$ | 540 | 100·00 | 100·00 | 100·00 | 99·80 |

The formula may also be written $3Ag^2S.Sb^2S^3$.

Pyrargyrite occurs also in Saxony, Norway, Hungary, at Guadalcanal in Spain, and in Cornwall. In Mexico it is worked extensively as an ore of silver. A *light-red silver ore* from Andreasberg was found by Zincken to be free from arsenic. A grey ore from the same locality contains both arsenic and antimony, and may be miargyrite (iii. 1010).

Pyrargyrite occurs like proustite (p. 739), changed to silver-glance, $Ag^2S^2$, also to pyrites. (Dana.)

**PYRELAÏN.** A name applied by Berzelius to the mobile oil obtained by distilling with water several of the empyreumatic oils resulting from the dry distillation of organic bodies, such as oil of wax, amber, bones, &c.

**PYRENAÏTE.** A variety of iron-lime-garnet (ii. 772), black or greyish-black, often with semi-metallic lustre.

**PYRENE.** $C^{15}H^{12}$? (Laurent, Ann. Ch. Phys. [9] lxvi. 136.)—A crystalline hydrocarbon, obtained, together with chrysene, by the dry distillation of fats, resins, and coal. To prepare it, the ethereal liquid which has served for the extraction of chrysene (i. 958), is exposed to the temperature of a freezing mixture; the pyrene is then deposited in the crystalline state.

Pyrene crystallises from alcohol in microscopic rhomboïdal laminæ, very much like anthracene. It is tasteless, inodorous, insoluble in water, slightly soluble in alcohol and in ether; melts between 170° and 180°, and solidifies in a crystalline foliated mass. At a higher temperature it volatilises without decomposition. It is carbonised by sulphuric acid. It gave by analysis 93·15 per cent. carbon and 6·11 hydrogen; the formula $C^{15}H^{12}$ requires 93·7 carbon and 6·3 hydrogen.

*Dinitropyrene*, $C^{15}H^{10}(NO^2)^2$, is formed by the action of warm nitric acid on pyrene, as a thick brown oil, which, after washing with water, dries up to a very brittle resin having the colour of gamboge but redder; it melts in boiling alcohol.

**PYRETHRIN.** This name was given by Parisel to a soft resin extracted by alcohol and ether from *Radix Pyrethri*, which however, according to Koene, is not a definite substance. The latter found in the root 0·25 per cent. of a resin insoluble in potash, 1·60 of a brown acrid oil soluble in potash, 0·35 of a yellow oil soluble in potash, 9·40 gum, 57·70 inulin, 7·60 salts, 19·80 vegetable fibre, and traces of tannic acid. The two oils and the resin together constitute Parisel's pyrethrin.

The flower-heads of *Pyrethrum carneum* which, when pulverised, form the "Persian insect-powder" contain, according to J. Hanamann (Vierteljahrs. pr. Pharm. xii. 522), neither a narcotic base nor santonin. The action of the powder is probably due to a pale yellow essential oil, which has a pungent odour, produces headache, and kills or stupefies small insects.

**PYRGOM.** A dingy variety of Sahlite. (See AUGITE, i. 474.)

**PYRIDINE.** $C^5H^5N$. (Anderson, Ed. Phil. Trans. xvi. 4; also xx. [2] 247; Phil. Mag. J. [4] ii. 257; Ann. Ch. Pharm. lxxx. 55; Jahresb. 1851, p. 478.—C. Grev. Williams, Phil. Mag. J. [4] viii. 24; also Ed. Phil. Trans. xxi. [2] 315; Chem. Gaz. Nov. 1, 1855.—Church and Owen, Chem. News, ii. 146; Phil. Mag. [4] xx. 110.)

A base discovered by Anderson in his investigation of bone-oil. Subsequently found by C. G. Williams among the bases in the tar obtained by distillation of the bituminous shale of Dorsetshire. Traces of a base having the same composition were observed by C. G. Williams among the alkaloïds produced by destructive distillation of cinchonine. Found by C. G. Williams in coal naphtha, also by Church and Owen in the tar of peat. It is produced artificially by the action of nascent hydrogen on azodinaphthyldiamine. (Perkin, Chem. Soc. J. xviii. 9.)

*Preparation.*—Precisely the same operations are necessary as in the case of picoline (p. 637), except that in the fractional distillation the portion distilling at 117° is to be collected instead of that which boils at 140°.

*Properties.*—Pyridine is a colourless mobile liquid, having a most powerful and peculiar odour closely resembling that of picoline, and, like that alkaloid, causing a bitter taste in the mouth and back of the throat. It fumes on the approach of a rod dipped in hydrochloric acid, even more strongly than picoline. Its solution in water behaves with bleaching powder like picoline. Its specific gravity at 0° is 0·9858. It precipitates the salts of zinc, iron, manganese, and aluminium in the cold, nickel-salts only on the application of heat, and the precipitate dissolves in excess. In solutions of copper it gives a pale blue precipitate, soluble in excess of base with a deep blue colour, not distinguishable from that produced by ammonia. It has a strong tendency to form crystallisable double salts. It boils steadily at about 117°. The density of its vapour was found to be 2·91; theory requires 2·734. The excess of the experimental over the theoretical numbers arose from the presence of traces of picoline. (Anderson.) The refractive indices of a specimen of pyridine from Dr. Hofmann's laboratory were found by Gladstone and Dale to be:—for A, 1·4940; D, 1·5030; H, 1·5387, the temperature at the time of the experiment being 21·5°.

Pyridine is soluble in water in all proportions, and is difficult to obtain absolutely dry. (Anderson.)

*Decompositions.*—Pyridine, like its homologues, is exceedingly stable and resists the action of oxidizing agents. It may be boiled with monohydrated *nitric acid*, or with *chromic acid* without decomposition, and treatment with nitric acid is to be resorted to as a means of purification when the base is contaminated with empyreumatic matters (Anderson).—1. *Chlorine* acts on pyridine in the same manner as on picoline (Anderson).—2. When *bromine-water* is gradually added to a solution of pyridine, the liquid becomes muddy, and, as the quantity of bromine increases, an abundant precipitate appears, and collects at the bottom of the vessel in the form of a reddish mass of a more or less resinous appearance. This substance is insoluble in water, but soluble in alcohol and ether. When boiled with water, it melts and emits an odour resembling that of bromine. Hydrochloric acid decomposes it, liberating bromine. Potash decomposes it also, liberating the base. From these reactions, Anderson concludes that the substance is a direct compound of pyridine with several atoms of bromine. Dry pyridine thrown into dry bromine-vapour solidifies to a crystalline mass which dissolves in water, leaving an insoluble matter probably analogous to the compound produced in the same manner by acting on pyridine or picoline with dry chlorine (Anderson).—3. When pyridine and tincture of *iodine* are mixed and evaporated to dryness on the water-bath, a dark brown mass is left, partially soluble in water, leaving some brown crystals; they are easily decomposed, and appear to be similar in character to the iodine-compounds of the fixed bases. The watery solution contains hydriodate of pyridine contaminated with a basic impurity which may be removed by animal charcoal. (Anderson.)

PYRIDINE SALTS. *Hydrochlorate of pyridine*, $C^5H^5N.HCl$.—When hydrochloric acid saturated with pyridine is evaporated on the water-bath, the syrupy fluid on cooling gradually becomes converted into a hard radiated mass of crystals. The salt deliquesces in moist air. It sublimes unchanged at a high temperature. It is soluble in alcohol, but less so than in water; insoluble in ether. (Anderson.)

*Acid sulphate of pyridine*, $C^5H^5N.H^2SO^4$.—When sulphuric acid is mixed with excess of pyridine and evaporated over the water-bath, a deliquescent crystalline mass is left, soluble in all proportions in water and alcohol, but insoluble in ether. (Anderson.)

*Hydriodate of pyridine*, $C^5H^5N.HI$.—Tabular crystals, readily soluble in alcohol and in water, but not deliquescent. (Anderson.)

*Hydrobromate of pyridine*, $C^5H^5N.HBr$.—A deliquescent salt obtained in acicular crystals on evaporating its solution. (Anderson.)

*Nitrate of pyridine*, $C^5H^5N.HNO^3$.—Easily obtained by mixing nitric acid and pyridine. If the acid be concentrated, and the base dry, or nearly so, much heat is evolved, and the mixture solidifies into a mass of short needles, which after pressure between folds of filtering paper, resembles loaf-sugar. The salt may be purified by recrystallisation from water or boiling spirit; the latter is to be preferred. On cooling it is deposited from an alcoholic solution in fine needles an inch long, even when operating on a very small scale. Sometimes it is obtained in short thick prisms. It is not deliquescent, but extremely soluble in water, less so in alcohol, insoluble in ether. Heated in a retort it melts, and, if the temperature be raised gradually, sublimes in a white woolly mass; but, if briskly heated, it distils in the form of a thick oily liquid, which solidifies to a mass of acicular crystals. Heated on a platinum knife, it takes fire, and burns with great brilliancy and a rapidity almost amounting to deflagration. (Anderson.)

*Chloraurate of pyridine*, $C^5H^5N.HCl.AuCl^3$.—A fine lemon-yellow crystalline powder, immediately deposited on adding solution of chloride of gold to a solution of hydrochlorate of pyridine. It dissolves readily in hot water, and is deposited on cooling in fine yellow needles, little soluble in cold water, and insoluble in alcohol. (Anderson.)

*Chloroplatinate of pyridine*, $2(C^5H^5N.HCl).Pt^{iv}Cl^4$.—A solution of the hydrochlorate of pyridine mixed with solution of tetrachloride of platinum, deposits flattened prisms easily soluble in boiling water, less soluble in alcohol, insoluble in ether.

*Products of decomposition of Chloroplatinate of Pyridine.*—When chloroplatinate of pyridine, free from excess of platinic chloride, is dissolved in hot water, and the solution kept boiling for five or six days, it is entirely converted into a substance resembling sublimed sulphur in appearance. It is insoluble in water and acids, but is decomposed on boiling with solution of hydrate of potassium, pyridine being evolved. The sulphur-like body is the hydrochlorate of a platinum-base analogous to platinamine; it has therefore received the name of *platino-pyridine*. Its formation consists simply in the expulsion of one atom of hydrochloric acid from one atom of the chloroplatinate, thus:—

$$2(C^5H^5N.HCl)Pt^{iv}Cl^4 \quad = \quad C^{10}H^6PtN^2.4HCl \ + \ 2HCl.$$

If the boiling be arrested before the entire conversion of the chloroplatinate into the salt just described, beautiful shining plates are deposited. They consist of a double salt formed by the union of one atom of the dihydrochlorate of platino-pyridine with one atom of the original platinum-salt. (Anderson.)

When chloroplatinate of pyridine is boiled with excess of pyridine, the liquid becomes dark coloured, and on evaporation to dryness in the water-bath, and addition of water, a dark solution is obtained, and a crystalline residue left. This substance is the hydrochlorate of another platinum-base, *platosopyridine*, analogous to platosamine. The salt has the formula $(C^5H^5N)^2.Pt''Cl^2$ or $C^{10}H^8PtN^2.2HCl$.

### *Substitution-derivatives of Pyridine.*

METHYL-PYRIDINE.—This compound has not yet been examined.

ETHYL-PYRIDINE.—The free bases of this class undergo decomposition when warmed. (See ETHYL-PICOLINE, p. 639.)

*Hydriodate of Ethyl-pyridine*, $C^7H^9N.HI$.—Obtained in the same manner as the corresponding picoline base, and of similar properties.

*Chloroplatinate of Ethyl-pyridine*, $2(C^7H^9N.HCl)Pt^{iv}Cl^4$.—Beautiful garnet-coloured rhomboïdal plates with bevelled edges, easily obtained a quarter of an inch in diameter, even when operating on very small quantities. (Anderson.) C. G. W.

**PYRITES.** A mineralogical name including various metallic sulphides, chiefly those of copper and iron.

Arsenical pyrites includes the two species, leucopyrite, $FeAs^2$, and mispickel, $FeAs^2.FeS^2$ (iii. 368).

Copper pyrites is $Cu^2S.Fe^2S^3$ (ii. 77).

Iron pyrites, $FeS^2$, includes the yellow or cubic species, and white iron pyrites or marcasite, which crystallises in trimetric forms (iii. 402). Varieties of the latter are: *Radiated pyrites*, including the radiated masses and more simple crystals; *spar pyrites*, the macled crystals; *hepatic pyrites*, the decomposed liver-brown monometric crystals originally consisting of yellow iron pyrites, also certain hexagonal pseudomorphs; *cockscomb pyrites*, the crest-like aggregations of marcasite; *cellular pyrites*, the cellular varieties formed by the decomposition of crystals of galena which contained films of pyrites between its layers.

Magnetic pyrites or pyrrhotin is generally $Fe^7S^8$ (iii. 402).

Tin pyrites is $Cu^2S(SnS^2.Fe^2S^3)$. See TIN.

Variegated pyrites or erubescite is $FeS.2Cu^2S$ (ii. 78).

The native sulphides of copper and iron are extensively used for the extraction of sulphur and the manufacture of sulphuric acid (see Richardson and Watts's *Chemical Technology*, vol. i. Pt. 3 and Appendix).

**PYROACETIC SPIRIT.** Syn. with ACETONE.

**PYROALIZARIC ACID.** Syn. with PHTHALIC ANHYDRIDE (p. 631).

**PYROBENZOLINE.** Syn. with LOPHINE (iii. 733).

**PYROCAMPHRETIC ACID.** $C^{10}H^{14}O^4$. (Schwanert, Ann. Ch. Pharm. cxxviii. 77; Jahresb. 1863, p. 397.)—An acid produced by the action of heat on camphretic acid, one of the products of the action of nitric acid on camphor. When camphor is heated with 10 or 12 pts. of nitric acid of specific gravity 1·34, the liquid cohobated as long as any action goes on, the product freed as completely as possible by repeated evaporation from camphoric acid (i. 730) which crystallises out, and from nitric acid, and the syrupy mother-liquor then treated with 10 pts. of cold water, camphretic acid, $C^{10}H^{14}O^{7} = \left.\begin{matrix}(C^{10}H^{11}O^{4})'''\\H^{3}\end{matrix}\right\}O^{3}$, dissolves, while another acid remains behind. To purify the product, the filtered solution is evaporated till the residue dissolves completely in cold water, and the solution is fractionally precipitated, either immediately or after neutralisation with ammonia, with neutral acetate of lead, which throws down the rest of the camphoric acid, together with a third acid. The solution filtered from these lead-salts is then completely precipitated with acetate of lead, the washed precipitate is decomposed by sulphydric acid, and the acid filtrate is evaporated. Camphretic acid is thus obtained as an inodorous, pale yellow, thick syrup, like Venice turpentine, having a sour, pungent, and somewhat bitter taste. It dissolves easily in water, alcohol, and ether, and forms uncrystallisable salts, having the general formula $C^{10}H^{11}M^{3}O^{7}$.

The *ethylic ether*, $C^{10}H^{11}(C^{2}H^{5})^{3}O^{7}$, obtained by decomposing the silver-salt with iodide of ethyl, or by passing hydrochloric acid gas into the alcoholic solution of the acid, is a non-volatile viscid oil of specific gravity 1·0775 at 13°. *Diethyl-camphretic acid*, $C^{10}H^{12}(C^{2}H^{5})^{2}O^{7}$, is produced, together with the neutral ether, by the last-mentioned process, and may be extracted by treating the oil separated by water with dilute soda-ley, agitating the neutralised solution with ether, and evaporating the ether. It then remains as a thick viscid oil of specific gravity 1·128 at 13°.

Camphretic acid subjected to slow distillation in an oil-bath yields at 100° an acid watery distillate containing acetic acid and acetone, then between 180° and 220° an oily distillate, which partly solidifies in tabular crystals, and finally at about 270° a white crystalline sublimate, with a large residue of charcoal. The oily body is pyrocamphretic acid, $C^{10}H^{14}O^{4}$; the tabular crystals are metacamphretic acid, $C^{10}H^{10}O^{6}$; the sublimate consists of camphoric anhydride, $C^{10}H^{14}O^{3}$.

Pyrocamphretic acid is a pale yellow viscid oil, heavier than water, having an aromatic odour, and a slightly sour, burning, aromatic taste. It boils between 206° and 210°, does not solidify at 0°, is insoluble in water, but dissolves in alcohol and ether, forming strongly acid solutions. The barium-salt and the lead-salt $C^{20}H^{22}Pb^{3}O^{8}$, are white amorphous precipitates.

Metacamphretic acid, $C^{10}H^{10}O^{3}$, crystallises from an alcoholic solution decolorised with animal charcoal, in rhombic tablets, which melt at 89°, solidify at 66°, dissolve sparingly in cold, easily in hot water, and in all proportions in alcohol and ether. The aqueous solution, which has an acid reaction, is not precipitated even after neutralisation, by calcium or barium-salts.

**PYROCATECHIN.**
**PYROCATECHUIC ACID.** } Syn. with OXYPHENIC ACID (p. 315).

**PYROCHLORE.** A mineral consisting of niobate and titanate of calcium, cerium, &c. (p. 57). Those varieties which contain fluorine without water were called by Hermann *fluochlore*, the others *hydrochlore*.

**PYROCITRIC ACIDS.** Acids produced by the destructive distillation of citric acid, viz. aconitic, citraconic, and itaconic acids. Mescaconic or citracartic acid, produced by the action of boiling dilute nitric acid on citraconic acid, is also included by Gerhardt under the same general denomination.

**PYROCHROÏTE.** A variety of brucite, with excess of manganese, found in the Pajsberg iron and manganese mine in Sweden, where it forms white nacreous veins in the magnetic iron ore. It is laminar, as hard as brucite, effloresces in the air, assuming first a bronze, then a black colour; when heated it becomes green, and afterwards black, with loss of water; contains 76·400 MnO, 0·006 FeO, 3 140 MgO, 1·270 CaO, 15·350 $H^{2}O$, and 3·834 $CO^{2}$. (Igelström, Pogg. Ann. cxxii. 181.)

**PYROCLASITE.** A mineral occurring in kidney-shaped masses in the Mongo islands on the Mosquito coast. It consists mainly of a hydrated tricalcic phosphate, $Ca^{3}P^{2}O^{8}.2H^{2}O$.

**PYROCONINE.** A basic poisonous substance said to be produced by the dry distillation of hemlock (Handw. vi. 709).

**PYRODEXTRIN.** (Gélis, Ann. Ch. Phys. [3] lii. 388.)—A product obtained by the roasting of starch (appearing indeed to be the only coloured substance thereby produced), of cereal grains, potatoes, maize, or coffee.—Starch is roasted, with constant stirring, in an open vessel strongly heated on one side, fresh portions being continually brought in contact with the hot part, till it is free from adhering water, swells up strongly, gives off pungent vapours, and sinters together, so that it is easily separated from the hot bottom of the vessel. It is then dissolved in hot water; the clear filtrate is evaporated; and the residue is dried and heated by small portions in an air-bath to 220°

—230°, to complete the roasting. The spongy product thus obtained is purified, especially from adhering dextrin, by repeatedly dissolving it in water and precipitating the solution with alcohol, as long as dark flakes continue to separate—or, in presence of a large quantity of dextrin, by precipitating the aqueous solution with excess of baryta-water containing alcohol, washing the resulting precipitate with weak spirit, pouring upon it a quantity of sulphuric acid sufficient to decompose it, filtering the liquid to remove sulphate of barium, and precipitating the filtrate with alcohol. The pyrodextrin, which separates in the form of syrup, is dissolved in a small quantity of water, the filtrate evaporated over the water-bath, and the residue dried at 140°.

Pyrodextrin is a solid, brown, friable mass, shining and tough when moist. Inodorous and tasteless. When dried at 160°, it gives by analysis 45·7 per cent. carbon and 6·2 hydrogen, which may be represented by the empirical formula $C^{48}H^{74}O^{37}$, requiring 46·37 C, 5·25 H, and 47·68 O.

*Combinations.*—Pyrodextrin when exposed to the air takes up 3 at. water, and afterwards dissolves readily in water, forming a brown adhesive gum. It is sparingly soluble in alcohol of 22 per cent.; insoluble in absolute alcohol and in ether. Aqueous pyrodextrin is not coloured purple-red by *iodine* (like dextrin), but is decolorised by moist hydrate of aluminum.

The aqueous solution mixed with baryta-water and weak alcohol yields a precipitate containing $C^{48}H^{72}Ba''O^{37}.Ba''O$; and with acetate of lead and absolute alcohol, a precipitate containing $C^{48}H^{72}Pb''O^{37}$.

*Decompositions.*—1. Pyrodextrin remains unaltered at 210°—220°, but decomposes at a higher temperature; takes fire with difficulty, and leaves a hard, coherent, slowly-burning cinder.—2. When treated with *nitric acid*, it yields oxalic acid.—3. By *oil of vitriol* or strong *hydrochloric acid*, it is converted into a sparingly soluble brown powder; dilute sulphuric or hydrochloric acid alters it but very slowly, even when heated.—4. It reduces cuprous oxide from an *alkaline solution of cupric oxide*, and from solutions of *gold* and *silver*-salts it reduces the metals.

**PYRODMALITE.** Syn. with Pyrosmalite.

**PYRO-ELECTRICITY.** Electricity developed by heat in crystals (ii. 411).

**PYROGALLEÏN.** An uncrystallisable product, formed by the action of ammonia on pyrogallic acid in open vessels. Its formation is probably analogous to that of orceïn from orcin:

$$\underset{\text{Pyrogallic acid.}}{3C^6H^6O^3} + 6NH^3 + O^9 = \underset{\text{Pyrogallein.}}{C^{18}H^{20}N^6O^{10}} + 8H^2O.$$

It forms brown precipitates with many metallic salts; but they decompose during washing. (Rosing, Compt. rend. xlvi. 1139.)

**PYROGALLIC ACID.** *Dioxyphenic acid*, $C^6H^6O^3$.—This acid was first observed by Scheele, and was considered as sublimed gallic acid. Berzelius and Pelouze established its composition. It contains the elements of gallic acid minus carbonic anhydride.

It is best prepared by heating a dried aqueous extract of nut-galls in a pot on which is placed a cap, such as is used in the sublimation of benzoic acid. The vessel is placed in a sand-bath and kept at a temperature of 180° to 185°, for 10 or 12 hours. In this way about 5 per cent. of acid is obtained. According to Liebig (Ann. Ch. Pharm. ci. 47), gallic acid is the best source of pyrogallic acid. The coarsely powdered gallic acid is mixed with twice its weight of bruised pumice, and placed in a retort in the tubulure of which is a tube connected with a carbonic acid apparatus. The advantage of this arrangement is that the pyrogallic acid, which decomposes almost at the same temperature as that at which it forms, is rapidly removed from the retort.

Pyrogallic acid is also produced, together with gallic (dioxysalicylic) acid by the action of hot caustic potash-solution on di-iodosalicylic acid. (Lantemann, Ann. Ch. Pharm. cxx. 299; Jahresb. 1861, p. 398.)

Pyrogallic acid crystallises in long flattened prisms soluble in 2½ pts. water at 12°, and somewhat less so in alcohol and ether.

It melts at 115° and boils at 210°, and its vapour excites coughing. At 250° it blackens, gives off water, and leaves an abundant residue of *metagallic acid*:

$$\underset{\text{Pyrogallic acid.}}{C^6H^6O^3} = \underset{\text{Metagallic acid.}}{C^6H^4O^2} + H^2O.$$

In the dry state it does not alter in the air, but its aqueous solution becomes brown, and leaves a black residue on evaporation. This change is most rapid in the presence of alkalis. When potash or soda is added to a solution of pyrogallic acid, the solution

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becomes rapidly black from absorption of oxygen, and if the liquid be evaporated, a black gummy residue of carbonate and acetate is obtained. It is on this rapid absorption of oxygen that the use of pyrogallic acid in endiometry is based. (See ANALYSIS OF GASES, i. 283.) According to Boussingault, Calvert and Cloez, however (Jahresb. 1863, p. 389), a small portion of the oxygen is converted into carbonic oxide, the volume of that gas amounting to 3—4 per cent. of that of the oxygen absorbed in an atmosphere of pure oxygen, and about 2½ per cent. in air.

Pyrogallic acid is easily oxidised by *permanganate of potassium*, and the reaction is used by Monier (Compt. rend. xlvi. 577; Jahresb. 1858, p. 629), for the volumetric estimation of the acid. It is not acted upon by hydrochloric acid. With fuming *sulphuric acid* it forms a brown solution containing a sulpho-acid not yet examined With fuming *nitric acid* it yields oxalic acid (Rosing). Its aqueous solution is turned brown by *nitrous acid*, even in very small quantity, so that in fact, pyrogallic acid affords as delicate a test for nitrous acid as iodised starch-paste (Schönbein, Zeitschr. anal. Chem. i. 319).—*Chlorine* turns pyrogallic acid black, and gives off hydrochloric acid. *Iodine* does not appear to act upon it below 200°. With anhydrous *bromine* it forms the compound $C^6H^3Br^3O^3$. It is not acted on by *ammonia-gas* in close vessels, but if exposed to the air at the same time, it is converted into pyrogalleïn (p. 758). (Rosing, Compt. rend. liv. 1149; Jahresb. 1857, p. 315.)

When pyrogallic acid is added to *milk of lime*, the liquid assumes a beautiful red tint, which rapidly passes to a deep brown. This reaction is so delicate as to serve for detecting small quantities of the acid.

The solution of a *ferrous salt* added to pyrogallic acid produces a beautiful indigo colour, the presence of the smallest trace of ferric salt produces a deep green tint. With *ferric salts* alone a red colour, but without a precipitate, is obtained. *Dichromate of potassium* produces a brown colour.

The salts of *mercury*, *silver*, *gold* and *platinum* are easily reduced to the metallic state by pyrogallic acid.

Pyrogallic acid is extensively used in photography as a reducing agent, and also in some processes for colouring the hair brown or black.

It is a weak acid. The addition of the smallest quantity of alkali gives it an alkaline reaction and colours it. It liberates carbonic acid from the alkaline carbonates, but not from the carbonates of the alkaline earths. According to Rosing, it does not decompose any carbonates.

The pyrogallates are little known. They are more soluble than the gallates, but like them, they have a strong tendency to become coloured in contact with the air. To prevent this alteration they should be evaporated in a vacuum.

The *potassium-salt* crystallises, according to Pelouze, in rhomboïdal plates. According to Rosing, on the other hand, pyrogallic acid does not form definite salts with ammonia or with the fixed alkalis.

The most stable of the pyrogallates is the *antimony-salt*, $C^6H^3SbO^4$, or rather $C^6H^3(SbO)'O^3$, which separates in white nacreous laminæ on mixing a somewhat concentrated solution of the acid with a boiling solution of tartar-emetic. It remains unaltered at 130°, is insoluble in water, but dissolves easily in hydrochloric acid (Rosing). A *lead-salt* containing $C^{12}H^{10}Pb''O^6.Pb''H^2O^2$ is precipitated on dropping a solution of neutral lead-acetate into an excess of pyrogallic acid. (Stenhouse, Ann. Ch. Pharm. xlv. 1.)

Pyrogallic acid also combines with *gelatin* and *casein*. When heated for 36 hours with stearic acid to 200°, it forms a crystalline compound which cannot be separated from the excess of stearic acid. (Rosing.)

*Tribromopyrogallic acid*, $C^6H^3Br^3O^3$.—Produced by the action of anhydrous bromine on dry pyrogallic acid, and separates from alcoholic solution in large crystals containing 1 at. water. It is nearly insoluble in cold water, decomposable by boiling water. The solution when mixed with alkalis, acquires a deep red colour, changing to brown on exposure to the air. Ferrous sulphate produces, even in a very dilute solution of the bromine-compound, a deep blue colour, turning black on prolonged exposure to the air. (Rosing.) E. A.

**PYROGEN.** A name applied by Dumas to pyro-acids and other products of the action of heat on organic bodies.

**PYROGENIC ACID.** Syn. with FORMIC ACID.

**PYROGLUCIC ACID.** Syn. with PYRODEXTRIN.

**PYROGLYCERIN.** Syn. with Diglycerin or Diglyceric alcohol. (See GLYCERYL, HYDRATES OF, ii. 894.)

**PYROGLYCIDE.** Syn. with Diglycide. $\left.\begin{matrix}(C^3H^5)^2\\ H^2\end{matrix}\right\}O^4$ (*loc. cit.*).

**PYROGLYCI-TRISULPHUROUS ACID.** $\left.\begin{matrix}(SO)^3\\ (C^3H^5)^2\\ H^2\end{matrix}\right\}O^7$.—An acid produced by the action of nitric acid on dithioglycerin or trithioglycerin (ii. 895). It is a gummy deliquescent mass. Its salts, formed by the substitution of $M^2$ or $M''$ for the basic hydrogen of the acid, are insoluble in alcohol, and with the exception of the lead-salt, deliquescent. The solution of the free acid evaporated with dilute nitric acid, yields glyceri-monosulphurous, oxalic, and sulphuric acids; with excess of nitric acid, only the two latter. (Carius, Ann. Ch. Pharm. cxxiv. 221.)

**PYROGNOMIC MINERALS.** Minerals which when heated to a certain degree, exhibit a glow or incandescence, probably arising from a new disposition of their molecules. Such is the case with gadolinite, orthite, pyrochlore, tachnewkinite, uranotantalite, euxenite, polycrase, malacone and a certain variety of sphene (Handw. d. Chem. vi. 62): see also AMORPHISM (i. 200).

**PYROGUAIACIC ACID.** Syn. with GUAIACOL (ii. 946).

**PYROGUAIACIN.** A crystalline substance produced, together with guaiacol, by the dry distillation of guaiăretic acid. See GUAIACUM (ii. 948).

**PYROLA.** *Pyrola* (or *Chimaphila*) *umbellata*, contains according to S. Fairbank, (Am. J. Pharm. xxxii. 254; Jahresb. 1860, p. 547), an iron-greening tannin, starch, gum, uncrystallisable sugar, pectic acid, resin, fat, chlorophyll, an acrid resinous substance, a yellow colouring matter, and a yellow crystalline body called chimaphyllin. The leaves (? dried) yield 5·24 per cent. ash.

On distilling the plant with water, chimaphyllin condenses in the neck of the retort (the stalks yield more than the leaves). It crystallises in long golden-yellow needles, tasteless, inodorous, sublimable without decomposition, insoluble in water, soluble in alcohol, ether, chloroform, and oils both fixed and volatile. The alcoholic solution is not precipitated by mercuric chloride or tannic acid.

**PYROLEIC ACID.** Syn. with SEBACIC ACID.

**PYROLIGNEOUS ACID.** Impure acetic acid obtained by the distillation of wood (i. 9).

**PYROLINE.** Syn. with PYRROL.

**PYROLITHOFELLIC ACID.** $C^{20}H^{34}O^3$.—An acid oil produced by the dry distillation of lithofellic acid, the chief constituent of some kinds of oriental bezoar (ii. 584). Lithofellic acid, $C^{20}H^{36}O^4$, is extracted from these concretions by solution in boiling alcohol, and crystallises, after decolorisation with animal charcoal, in very small rhomboïdal prisms, colourless, hard and easily pulverised. It dissolves in 29 pts. alcohol at 20°, and in 6½ pts. boiling alcohol; in 444 pts. cold ether and 47 pts. boiling ether. It melts at 205°, volatilises in white aromatic vapours when melted in an open vessel, and is converted by dry distillation, with loss of 1 at. water, into pyrolithofellic acid.

**PYROLIVILIC ACID.** $C^{20}H^{26}O^5 = 2C^{10}H^{12}O^2.H^2O$. (Sobrero, Ann. Ch. Pharm. liv. 206; Gm. xiv. 206.)—A product of the dry distillation of olivil (p. 200). It is a colourless oil, heavier than water, having the taste and smell of eugenic acid; boils above 200°. It is very slightly soluble in water, but easily soluble in alcohol and in ether. The aqueous solution reddens litmus. The oil dissolves chloride of calcium, and cannot again be separated therefrom. It dissolves readily in caustic potash, but without yielding a crystallisable salt (thereby distinguished from eugenic acid). The acid reduces nitrate of silver, and is converted by nitric acid into picric acid and a resin.

The alcoholic solution of the acid forms with basic acetate of lead, white curdy flakes which dissolve in alcohol and are separated from the solution by evaporation or by dilution with water. When separated by evaporation, they contain 57·6 per cent. lead-oxide; when precipitated by water, 53·2 per cent., the former agreeing with the formula $C^{10}H^{12}O^2.Pb''O$.

**PYROLUSITE.** Native peroxide of manganese (iii. 811).

**PYROMALIC ACID.** Syn. with MALEIC ACID (iii. 784).

**PYROMARIC ACID.** An acid obtained by subjecting pimaric acid (p. 645) to dry distillation: probably identical with sylvic acid (Laurent: see *Gmelin's Handbook*, xvii. 325).

**PYROMECONIC ACID.** $C^5H^4O^3$. *Pyrocomenic acid.*—An acid isomeric with

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pyromucic acid and citraconic anhydride, produced by the dry distillation of comenic or of meconic acid:

$$\underset{\text{Meconic acid.}}{C^7H^4O^7} = CO^2 + \underset{\text{Comenic acid.}}{C^6H^4O^5}; \text{ and } \underset{\text{Comenic acid.}}{C^6H^4O^5} = CO^2 + \underset{\text{Pyromeconic acid.}}{C^5H^4O^3}.$$

It was discovered by Sertürner in 1817, but regarded as identical with meconic acid, till the difference was pointed out by Robiquet in 1833. It has been chiefly studied by Robiquet (Ann. Ch. Phys. [2] v. 282; li. 236), Stenhouse (Phil. Mag. [3] xxiv. 128), and J. F. Brown (Phil. Mag. [4] iv. 161; viii. 201).

Pyromeconic acid is prepared by subjecting meconic acid to dry distillation, between 260° and 320°, pressing the semifluid distillate between paper, and purifying it by sublimation. It forms large transparent tables, dissolves easily in *water* and in *alcohol*, melts at 120°—125° and sublimes easily even below 100°. Its aqueous solution is coloured red by *ferric salts*. It is easily oxidised by *nitric acid* and by excess of *chlorine-water*, and converted into oxalic acid. With *bromine-water* it yields bromopyromeconic acid. It is not acted upon by iodine, but *chloride of iodine* converts it into iodopyromeconic acid.

Pyromeconates. Pyromeconic acid is monobasic. It is a very weak acid, does not decompose carbonates, and does not appear to form definite salts with the alkalis, inasmuch as an alkaline solution of the acid in potash or ammonia deposits free pyromeconic acid when left to evaporate.

The *barium-salt*, $C^{10}H^6Ba''O^6.H^2O$, and the *calcium-salt* $C^{10}H^6Ca''O^6.H^2O$, separate in slender needles when a solution of the acid supersaturated with ammonia is mixed with acetate of barium or calcium.—The *strontium-salt*, $C^{10}H^6Sr''O^6.H^2O$, separates on mixing alcoholic nitrate of strontium with an alcoholic and ammoniacal solution of pyromeconic acid, as a white crystalline powder, and may be obtained in stellate groups of needles by crystallisation from water. The *cupric salt*, $C^{10}H^6Cu''O^6$, is formed by boiling the aqueous acid with excess of cupric hydrate, and separates from the filtrate on cooling in long, slender, emerald-green, very fragile needles. It may also be obtained by mixing ammoniacal cupric sulphate with a warm aqueous solution of pyromeconic acid.—The *ferric salt*, $C^{30}H^9Fe'''O^{18}$, is deposited in vermilion-coloured crystals on adding ferric chloride to a hot concentrated solution of the acid.—The *lead-salt*, $C^{10}H^6Pb''O^6$, prepared like the barium-salt, is a white crystalline powder.—The *magnesium-salt*, $C^{10}H^6Mg''O^6$, is a white amorphous precipitate, obtained on mixing the warm aqueous solution of the acid with acetate of magnesium.—The *silver-salt* is obtained on adding nitrate of silver to the aqueous acid, as a yellow gelatinous precipitate, moderately soluble in water and in alcohol.

No ether or amide of pyromeconic acid has yet been obtained.

**Bromopyromeconic acid,** $C^5H^3BrO^3$, is obtained by adding bromine-water to the aqueous solution of pyromeconic acid, care being taken to avoid an excess of bromine, as that would produce oxalic acid. Bromopyromeconic acid separates from the solution on standing, in colourless prisms slightly soluble in cold, more soluble, with acid reaction, in boiling water, easily soluble in boiling alcohol, which deposits it by slow cooling in shortened prisms. It is coloured dark red-purple by ferric salts, dissolves without alteration in sulphuric acid, but is decomposed, with effervescence, by nitric acid. When distilled it gives off hydrobromic acid, and if the heat be continued, yields a crystalline sublimate.

It is monobasic, does not precipitate or reduce nitrate of silver, and gives no precipitate with barium-, calcium-, or magnesium-salts, even in presence of ammonia. With a hot solution of ammoniacal cupric sulphate it forms a bluish precipitate. The *lead-salt*, $C^{10}H^4Br^2Pb''O^6$ ( + $H^2O$ according to Brown), is obtained on mixing the hot alcoholic solutions of pyromeconic acid and acetate of lead, as a white precipitate composed of small needles which quickly decompose. It is insoluble in water and in alcohol.

**Iodopyromeconic acid,** $C^5H^3IO^3$. (J. F. Brown, Phil. Mag. [4] viii. 201.) —Produced by the action of protochloride (or protobromide) of iodine in aqueous solution on a cold saturated solution of pyromeconic acid. It crystallises in shining laminæ, melts when heated above 100°, forming a black liquid, which then suddenly decomposes, giving off a large quantity of iodine. Nitric acid decomposes it, with separation of iodine. When treated with excess of chloride of iodine it yields yellow hexagonal plates which were regarded by Brown as a peculiar substance, *iodomecone*, $C^6H^4I^6O^3$, but probably consist of iodoform (iii. 311).

Iodopyromeconic acid dissolves sparingly in cold water and alcohol, abundantly in both liquids at the boiling heat. The aqueous solution imparts a deep purple colour to ferric chloride, and forms with nitrate of silver a yellowish-white precipitate soluble in ammonia.

The alcoholic solution of the acid mixed with ammonia forms with acetate of barium a crystalline salt having the composition $C^{10}H^4I^2Ba''O^6.H^2O$. The *lead-salt*, $C^{10}H^4I^2Pb''O^6$, obtained in like manner, is an amorphous precipitate.

**PYROMELINE.** Hydrated sulphate of nickel, occurring in capillary interlacing crystals, or as a greenish-white efflorescence, at Wallace Mine, Lake Huron, on a sulphide of nickel and iron; also as an earthy pale yellow crust at the Frerichs Mine near Bayreut. (Dana, ii. 386.)

**PYROMELLITIC ACID.** $C^5H^2O^4$ or $C^{10}H^6O^8$? (Erdmann, Ann. Ch. Pharm. lxxx. 281.)—Produced by distilling mellitic acid at as low a temperature as possible. It then either sublimes in white crystals, or distils over as an oil which solidifies in a crystalline mass on cooling. Carbonic anhydride is given off at the same time, together with a little carbonic oxide, and a carbonaceous residue is left:

$$2C^4H^2O^4 = C^5H^2O^4 + 3CO + H^2O$$

or more probably

$$3C^4H^2O^4 = C^{10}H^6O^8 + 2CO^2.$$

It may also be obtained by distilling a mellitate, the copper or sodium-salt for example, with sulphuric acid; but the best mode of preparing the pure crystallised acid is to decompose the sodium-salt, purified by crystallisation from alcohol, with hydrochloric or nitric acid.

Pyromellitic crystallises in colourless triclinic prisms, exhibiting according to Naumann, the combination $oP : \infty P' . \infty' P . P_{,} . {}_{,}P . \bar{P}\infty . 2\bar{P}\infty$. Angle $oP : \infty P' =$ 111°; $oP : \infty' P =$ 94° 15′; $\infty' P : \infty P' =$ 76° 30′; $oP : {}_{,}P =$ 62°; $oP : P_{,} =$ 71° 45′; $\infty' P : P_{,} =$ 73°; $\infty P' : P_{,} =$ 140° 45′; $\infty P : {}_{,}P =$ 147° 45′; $oP : \infty\bar{P}\infty =$ 99° 45′; $oP : 2\bar{P}\infty =$ 76° 30′: $\infty\bar{P}\infty$ $2\bar{P}\infty =$ 156° 45′. The crystals are slightly soluble in cold water, very soluble in boiling water and in alcohol.

The acid dried at 100°—120° exhibits the following composition:

| | Erdmann. | $C^{10}H^6O^8$ | $C^{10}H^2O^4$ |
|---|---|---|---|
| Carbon . . . . . | 47·27—47·81 | 47·24 | 47·6 |
| Hydrogen . . . . . | 2·34— 2·41 | 2·37 | 1·6 |
| Oxygen . . . . . | „ „ | 50·39 | 50·8 |
| | | 100·00 | 100·0 |
| | | $+2H^2O$ | $+H^2O$ |
| Water of crystallisation . . | 12·33—12·53 | 12·41 | 12·5 |

The formula $C^{10}H^6O^8$ accords best with the analysis, and also accounts most readily for the formation of the acid (*vid. sup.*).

The crystals heated to 100° give off 12·5 per cent. water; at a higher temperature the acid melts and sublimes with partial decomposition; the melted acid if strongly heated, takes fire and burns with a bright smoky flame. The acid dissolves without decomposition in hydrochloric, nitric, and sulphuric acids at the boiling heat, and is precipitated by water from the last-mentioned solution.

According to the formula $C^{10}H^6O^8$, pyromellitic acid is tetrabasic, the formula of its normal salts being $\left.\begin{matrix}(C^{10}H^2O^4)^{iv} \\ M^4\end{matrix}\right\}O^4$. The pyromellitates of the alkali-metals are colourless, crystallisable, very soluble in water, insoluble in strong alcohol, slightly soluble in weak spirit. Their solutions precipitate a large number of metallic salts, the precipitates being very apt to retain alkali, to avoid which it is best to pour the alkaline pyromellitate into an excess of a hot solution of the metallic salt. The *barium-*, *calcium-*, *lead-*, and *silver-salts* are white crystalline precipitates. The *lead-salt* gave by analysis 65·34 and 65·23 per cent lead-oxide, the formula $C^{10}H^2\overset{''}{P}b^2O^8.H^2O$, requiring 65·49 per cent.—The silver-salt gave 67·7 to 68·0 per cent. $Ag^2O$; the formula $C^{10}H^2Ag^4O^8$ requires 68·0 per cent.

**PYROMERIDE.** A granitoïd rock containing felspathic spherules thickly disseminated. (Dana, ii. 246.)

**PYROMETER.** An instrument for measuring high temperatures. (See HEAT, iii. 20.)

**PYROMORINTANNIC ACID.** Syn. with OXYPHENIC ACID (p. 315).

**PYROMORPHITE.** Native Phosphato-chloride of lead. (See PHOSPHATES, p. 567.)

**PYROMUCAMIDE.** See PYROMUCIC ACID, AMIDES OF (p. 764).

**PYROMUCIC ACID.** $C^5H^4O^3 = \left.\begin{matrix}C^5H^3O^2\\ H\end{matrix}\right\}O$, or $\left.\begin{matrix}(C^5H^2O)'''\\ H\end{matrix}\right\}O^2$, or $\left.\begin{matrix}(C^5H^2O)''\\ H^2\end{matrix}\right\}O^2$. *Pyroschleimsäure. Brenzschleimsäure.*—This acid, metameric with pyromeconic acid and citraconic anhydride, was discovered by Scheele in 1780, but regarded at that time as succinic acid. It was first recognised as a distinct acid by Houton-Labillardière (Ann. Ch. Phys. [2] ix. 365), and has been further examined by Pelouze (Ann. Ch. Pharm. ix. 273); Boussingault (*ibid.* xv. 184); Liès-Bodart (*ibid.* c. 327); Schwanert (*ibid.* cxiv. 63; cxvi. 257); and by Schmelz and Beilstein (*ibid.* Suppl. iii. 275).

It is produced by the dry distillation of mucic acid:

$$C^6H^{10}O^8 = C^5H^4O^3 + CO^2 + 3H^2O;$$

and by the oxidation of furfurol, $C^5H^4O^2$, which is its aldehyde.

Its relations to furfurol and to bases are sufficiently represented by the first rational formula above given; but its relations to carbopyrolamide and carbopyrrolic acid (p. 764), are better expressed by the second or third.

*Preparation.*—1. Mucic acid is subjected to dry distillation; the distillate is mixed with water, filtered, and evaporated to the crystallising point; and the product is purified by recrystallisation, distillation or sublimation.—2. Furfurol is boiled with water and recently precipitated silver-oxide; the silver is precipitated from the filtrate by hydrochloric acid; the liquid again filtered and evaporated to the crystallising point; and the acid, which usually has a green colour, is purified by recrystallisation from dilute alcohol (Schwanert).—3. An alcoholic solution of furfurol mixed with a solution of potash in absolute alcohol, solidifies to a crystalline mass of potassic pyromucate, from which the acid may be obtained by distillation with hydrochloric acid (Ulrich, Zeitschr. Ch. Pharm. 1861, p. 186). Part of the pyromucic acid is converted at the same time into pyromucic alcohol. (Schmelz and Beilstein, p. 765.)

*Properties.*—Pyromucic acid forms white needles or laminæ which melt at 130°, and sublime easily even below 100°. It dissolves in 28 pts. of cold, and 4 pts. of boiling water, and is easily soluble in alcohol.

*Decompositions.*—1. Pyromucic acid is not attacked by nitric acid.—2. By *sulphuric anhydride* it is converted into sulphopyromucic acid, $C^5H^4SO^6$.—3. With *pentachloride of phosphorus* it yields chloride of pyromucyl, $C^5H^3O^2Cl$.—4. By *bromine*, in presence of water, it is converted first into a heavy oil (probably $C^4H^2O^3$), which appears to have been previously noticed by Cahours (*Gm. Handb.* x. 384), and ultimately into mucobromic acid, $C^4H^2Br^2O^3$:

$$C^5H^4O^3 + Br^8 + 2H^2O = C^4H^2Br^2O^3 + CO^2 + 6HBr.$$

With *chlorine* in like manner it yields mucochloric acid, $C^4H^2Cl^2O^3$. (Schmelz and Beilstein.)

Pyromucates. Pyromucic acid is monobasic. It dissolves zinc and iron with evolution of hydrogen.

The pyromucates of the alkali-metals are easily soluble in water and alcohol, and difficult to crystallise. The *potassium-salt*, $C^5H^3KO^3$, separates after a while from its alcoholic solution mixed with ether, in brilliant scales and needles permanent in the air. The *sodium-salt*, $C^5H^3NaO^3$, resembles the potassium-salt and may be crystallised in like manner. (Schmelz and Beilstein.)

The *barium-salt*, $C^{10}H^6Ba''O^6$, forms small crystals soluble in water and in alcohol (Schwanert). The *calcium-salt*, $C^{10}H^6Ca''O^6$, is obtained, by neutralising the aqueous acid with marble and evaporating, in small crystals, easily soluble in water and in alcohol. When prepared like the potassium-salt, it forms a snow-white crystalline powder. (Schmelz and Beilstein.)

The *cupric salt*, obtained by neutralisation, forms small green crystals, $C^{10}H^6Cu''O^6.6H^2O$, more soluble in hot than in cold water.

The *lead-salt*, $C^{10}H^6Pb''O^6.2H^2O$, separates from a concentrated aqueous solution on cooling in beautiful white hard crystals, sparingly soluble in cold, more soluble in hot water. (Schmelz and Beilstein.)

The *silver-salt*, $C^5H^3AgO^3$, forms white crystalline scales, but is partly decomposed during the evaporation of its aqueous solution.

### *Appendix to Pyromucic Acid.*

1. **Mucobromic acid,** $C^4H^2Br^2O^3$.—To prepare this acid, bromine is slowly added to pyromucic acid covered with a little water in a cooled vessel till it no longer disappears; and the product is digested with excess of bromine over the water-bath, till the heavy oil produced in the first stage of the reaction (p. *vid. sup.*) is wholly converted into mucobromic acid. The solution concentrated at the heat of the water-bath yields

mucobromic acid in tufts of white nacreous crystalline laminæ, much more soluble in hot than in cold water, easily soluble in alcohol, melting at 120°, and subliming with partial decomposition.

Mucobromic acid reddens litmus paper and decomposes carbonates, but its salts are very unstable. A solution of the acid in absolute alcohol digested for some time with hydrochloric acid, yields on addition of water, oily drops probably consisting of ethylic mucobromate.

When mucobromic acid is boiled with excess of baryta-water in a close vessel, carbonate of barium is precipitated, gaseous bromacetylene is given off, and a solution is formed containing bromide and muconate of barium. The reaction is,

$$\underset{\text{Mucobromic acid.}}{2C^4H^2Br^2O^3} + H^2O = \underset{\text{Muconic acid.}}{C^4H^2O^3} + \underset{\text{Brom-acetylene.}}{C^2HBr} + 2CO^2 + 3HBr.$$

Boiled with *oxide of silver*, it yields a silver-salt having the composition $C^7H^2Br^3Ag^3O^5$, the reaction probably taking place as shown by the equation,

$$2C^4H^2Br^2O^3 + 2Ag^2O = C^7H^2Br^3Ag^3O^5 + AgBr + H^2O + CO^2.$$

This silver-salt decomposed by sulphuretted hydrogen yields a crystallised acid, $C^7H^5Br^3O^5$, which, when boiled with baryta, is resolved into muconic acid, bromacetylene, hydrobromic acid and carbonic anhydride:

$$C^7H^5Br^3O^5 = C^4H^2O^3 + C^2HBr + 2HBr + CO^2.$$

The ultimate products are therefore the same as when mucobromic acid itself is treated with baryta-water. (Schmelz and Beilstein.)

2. **Mucochloric acid,** $C^4H^2Cl^2O^3$, is prepared by passing chlorine gas into a warm aqueous solution of pyromucic acid, and concentrating the liquid, first over the water-bath, then over oil of vitriol and lime. It forms small, shining, limpid crystals, easily soluble in water and alcohol, and melting at 125°. (Schmelz and Beilstein.)

3. **Muconic acid,*** $C^4H^2O^3$.—When the liquid obtained as above by the action of baryta-water on mucobromic acid is freed from excess of baryta by means of carbonic acid, and the filtrate is evaporated, *muconate of barium* is deposited in crystalline crusts which may be purified by washing with cold and recrystallisation from hot water, or better by precipitation with alcohol. It then forms white flakes, consisting of $2C^4Ba''O^3.H^2O$. Its aqueous solution mixed with neutral acetate of lead, yields a white precipitate of *muconate of lead*, which dissolves in boiling water, and separates in small crystals on cooling. By decomposing this lead-salt with sulphuretted hydrogen, and evaporating the filtrate, *muconic acid* may be obtained in crystals. This acid, so far as its empirical formula is concerned, is homologous with pyromucic acid. (Schmelz and Beilstein.)

**PYROMUCIC ACID, AMIDES OF.** 1. *Pyromucamide*, $C^5H^5NO^2$ = $\left.\begin{matrix}C^5H^3O^2\\H^2\end{matrix}\right\}N$ or $\left.\begin{matrix}(C^5H^3O)'''\\H^2\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$ or $\left.\begin{matrix}H\\(C^5H^3O)''\\H^2\end{matrix}\right\}\begin{matrix}O\\N\end{matrix}$.—Produced by the action of ammonia on pyromucic chloride (Liès-Bodart), or by heating ethylic pyromucate with strong aqueous ammonia for some time to 120° (Schwanert). It is crystallisable, melts at about 130°, and sublimes easily without decomposition. It is soluble in water and in alcohol.

2. *Carbopyrrolic acid*, $\left.\begin{matrix}H^2\\(C^5H^3O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—This compound, metameric with pyromucamide, and related to it in the same mannner as alanine (lactamic acid) to lactamide (iii. 453), or glycocine (glycollamic acid) to glycollamide (ii. 902, 908), is obtained as a barium-salt by boiling carbopyrrolamide with excess of baryta as long as ammonia continues to escape, removing the excess of baryta by carbonic acid, and evaporating; carbopyrollate of barium then separates on cooling in large crystalline laminæ, and the aqueous solution of this salt decomposed by strong hydrochloric acid deposits carbopyrrolic acid in small white prisms. It sublimes at about 190° and decomposes at a slightly higher temperature into carbonic anhydride and pyrrol: $C^5H^5NO^2 = CO^2 + C^4H^5N$. It is quickly decomposed by acids, yielding, instead of pyrrol, the products of decomposition of that substance, namely ammonia and pyrrol-red.

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* This name is also applied to an acid having the composition $C^6H^8O^4$, produced by the action of nascent hydrogen on the acid $C^6H^4Cl^2O^4$, which latter results from the action of pentachloride of phosphorus on mucic acid. (Bude, Ann. Ch. Pharm. cxxxii. 95.) See APPENDIX.

*Carbopyrrolate of barium*, $C^{10}H^8Ba''N^2O^4$, forms large white laminæ, soluble in water and in alcohol.—The *lead-salt*, $C^{10}H^8Pb''N^2O^4$, obtained by decomposing the barium-salt with excess of lead-hydrate, is very soluble in water, and remains in nacreous crystalline scales when the solution is evaporated.

3. *Dipyromucamide* or *Carbopyrrolamide*, $C^5H^6N^2O$ $= \left.\begin{matrix} H \\ (C^5H^3O)''' \\ H^2 \end{matrix}\right\}N^2$ $= \left.\begin{matrix} H^2 \\ (C^5H^2O)'' \\ H^2 \end{matrix}\right\}N^2$.—This compound was first obtained by Malaguti (Ann. Ch. Pharm. c. 327). by the distillation of mucate of ammonium (or mucamide), and has since been more fully examined by Schwanert (*ibid.* cxvi. 270). Its formation from mucate of ammonium is represented by the equation:

$$C^6H^8(NH^4)^2O^8 \;=\; C^5H^6N^2O + CO^2 + 5H^2O.$$

Part of the product is, however, resolved into ammonia and pyrrol (p. 783). To prepare it, mucate of ammonium is subjected to dry distillation; the oily layer of pyrrol which floats on the watery distillate is removed; the solution, containing dipyromucamide and carbonate of ammonium, is evaporated over the water-bath; and the dipyromucamide is extracted from the crystalline residue by alcohol, and purified by recrystallisation from the same liquid, with addition of animal charcoal.

Dipyromucamide forms white, shining laminæ, easily soluble in alcohol and ether, less soluble in water. At 173° it melts to a liquid which solidifies to a crystalline mass at 133°. When boiled in aqueous solution with excess of baryta, it is resolved into ammonia and carbopyrrolic acid:

$$C^5H^6N^2O + H^2O \;=\; NH^3 + C^5H^5NO^2.$$

**PYROMUCIC ALCOHOL.** A compound related to pyromucic acid in the same manner as benzylic alcohol, $C^7H^8O$, to benzoic acid, $C^7H^6O^2$, and produced (together with pyromucic acid) by the action of alcoholic potash on furfurol, just as benzylic alcohol is produced from bitter almond oil. It is, however, more easily produced by the action of sodium-amalgam on furfurol. It is a brown-red oily liquid, nearly insoluble in water, very easily soluble in alcohol and ether, decomposed by distillation, converted by alkalis into pyromucic acid. (Schmelz and Beilstein, Ann. Ch. Pharm. Suppl. iii. 275.)

**PYROMUCIC CHLORIDE.** $C^5H^3O^2Cl$.—Produced by distilling pyromucic acid with pentachloride of phosphorus. It is a liquid which boils at 170°, is converted by water into pyromucic acid, and by ammonia into pyromucamide. (Liès-Bodart.)

**PYROMUCIC ETHERS.** *Ethylic Pyromucate*, $C^5H^3(C^2H^5)O^3$, is obtained by distilling pyromucic acid with alcohol and hydrochloric acid (Malaguti). It forms a lamino-crystalline mass, melting at 34°, boiling between 208° and 210°, easily soluble in alcohol and ether, insoluble in water. With ammonia it forms pyromucamide.

2. When this ether is subjected to the action of dry chlorine gas, it takes up 4 at. chlorine, without evolution of hydrochloric acid, and forms chloropyromucic ether, $C^5H^3Cl^4(C^2H^5)O^3$, a fragrant syrupy liquid, easily soluble in alcohol and ether, insoluble in water, and decomposing when heated, with abundant evolution of hydrochloric acid. With the fixed alkalis or ammonia it yields alcohol and a metallic chloride. (Malaguti.) The acid corresponding to this chlorinated ether has not yet been obtained.

**PYROPE.** Bohemian garnet containing chromium (ii. 772). Moberg supposes the chromium to be in the state of chromous oxide, and gives, as the result of analysis, 41·35 per cent. $SiO^2$, 22·35 $Al^2O^3$, 9·94 FeO, 4 17 CrO, 15·00 MgO, and 5·29 CaO.

**PYROPECTIC ACID.** A black substance produced by the action of heat on pectic, parapectic, or metapectic acid (p. 369).

**PYROPHORUS** (from πῦρ and φέρειν).—This term, in its widest sense, denotes any substance capable of taking fire spontaneously, or on very slight elevation of temperature, as is the case with phosphorus, phosphoretted hydrogen, cacodyl, &c.; but it is more commonly restricted to finely divided solid bodies which exhibit this property, such as metallic iron reduced from the oxide by ignition in hydrogen. The spontaneous inflammability of such bodies is due, partly to their powerful attraction for oxygen, partly to their pulverulent state, which enables them to condense the air rapidly within their pores, thereby causing a considerable rise of temperature, while at the same time they present a large surface to the action of the oxygen. When a solid mass of iron is exposed to the air, the heat developed by the oxidation of the

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superficial particles is at once conducted away throughout the entire mass, so that the temperature cannot rise sufficiently for the oxidation to go on; but when the metal is reduced to a heap of very fine particles, large numbers of these come into contact with the air at the same instant, and the heat developed by their oxidation is not conducted away to others which take no part in the action (see COMBUSTION, i. 1095).

The pyrophoric character is exhibited by all the more easily oxidable metals, which are reduced by hydrogen at temperatures below that at which their particles fuse or weld together, *e.g.* iron, nickel, cobalt, and manganese; also by the mixtures of finely divided metal and carbon obtained by igniting the tartrates, citrates, oxalates, and other organic salts of lead, iron, and some other metals. Tartrate or citrate of lead, when ignited in a glass tube as long as gaseous matter is evolved, and then left to cool, takes fire instantly on being thrown out into the air. The sulphides of potassium, sodium, and lithium, obtained by igniting the corresponding sulphates with lamp-black, and the alum-pyrophorus or Homberg's pyrophorus, produced by heating alum with lamp-black, starch, or flour, likewise exhibit spontaneous inflammability. (Handw. d. Chem. vi. 718.)

**PYROPHOSPHAMIC ACIDS.** Gladstone in 1849 (Chem. Soc. Qu. J. iii. 135), by subjecting chloronitride of phosphorus (p. 517) to the action of alkalis, obtained two tribasic acids, to which he assigned the formulæ $P^2NH^3O^4$ and $P^2N^2H^5O^4$, the first, called *azophosphoric acid*, consisting of phosphoric acid + PN, and the second called *deutazophosphoric acid*, or phosphoric acid + 2PN. Laurent, however (Compt. Chim. 1850, p. 387), suggested that these acids were amic acids derived from pyrophosphoric acid, the first being *pyrophosphamic acid*, $P^2NH^5O^6$, and the second *pyrophosphodiamic acid*, $P^2N^2H^6O^5$; and these formulæ have been confirmed by the more recent analyses of Gladstone and Holmes (Chem. Soc. J. xvii. 225). Lastly, Gladstone (*ibid.* xix. 1) has completed the series by the discovery of *pyrophosphotriamic acid*, $P^2N^3H^7O^4$. The relations of these acids to pyrophosphoric acid may be exhibited as follows:

| | | | |
|---|---|---|---|
| Pyrophosphoric acid . . . . . . | $P^2H^4O^7$ | | $= \left.\begin{matrix}(P^2O^3)^{iv}\\ H^4\end{matrix}\right\}O^4$ |
| Pyrophosphamic acid . . | $P^2NH^5O^6$ | $= P^2(NH^2)H^3O^6$ | $= \left.\begin{matrix}H^2\\ (P^2O^3)^{iv}\\ H^3\end{matrix}\right\}\begin{matrix}N\\ O^3\end{matrix}$ |
| Pyrophosphodiamic acid . . | $P^2N^2H^6O^5$ | $= P^2(NH^2)^2H^2O^5$ | $= \left.\begin{matrix}H^4\\ (P^2O^3)^{iv}\\ H^2\end{matrix}\right\}\begin{matrix}N^2\\ O^2\end{matrix}$ |
| Pyrophosphotriamic acid . . | $P^2N^3H^7O^4$ | $= P^2(NH^2)^3HO^4$ | $= \left.\begin{matrix}H^6\\ (P^2O^3)^{iv}\\ H\end{matrix}\right\}\begin{matrix}N^3\\ O\end{matrix}$ |
| | | or rather $P^2(NH)^3H^4O^4$ | $= \left.\begin{matrix}H^3\\ (P^2O^3)^{iv}\\ H^4\end{matrix}\right\}\begin{matrix}N^3\\ O\end{matrix}$ |

Pyrophosphamic acid is tribasic, and pyrophosphodiamic acid is dibasic, as indicated by their formulæ; but pyrophosphotriamic acid, which from analogy might be expected to be monobasic, is in reality tetrabasic, being capable of yielding di-, tri-, and tetrametallic as well as monometallic salts: hence it is best represented by the formulæ in the last line of the preceding table.

1. **Pyrophosphamic acid,**—$P^2NH^5O^6$.—This acid is produced from pyrophosphodiamic acid by simply heating its aqueous solution:

$$P^2N^2H^6O^5 + H^2O = P^2NH^5O^6 + NH^3;$$

but the decomposition is apt to go too far, yielding ultimately nothing but phosphate of ammonium. The metallic pyrophosphamates, however, are more stable, and those which are insoluble in dilute acids, the ferric or cupric salt for example, are easily prepared by heating an alkaline pyrophosphodiamate with an acid solution of the metal:

$$\underset{\text{Pyrophosphodiamate.}}{P^2N^2H^4M^2O^5} + MCl + H^2O = \underset{\text{Pyrophosphamate.}}{P^2NH^2M^3O^6} + NH^4Cl.$$

By decomposing the silver-salt with hydrochloric acid and evaporating the filtrate, pyrophosphamic acid is obtained as a semisolid, non-crystalline mass, having an acid reaction, deliquescing in moist air, soluble in alcohol, and capable of bearing a strong heat without decomposition.

*Pyrophosphamate of Ammonium* is obtained as a gummy mass by decomposing the lead-salt with somewhat less than an equivalent quantity of ammonia, and evaporating the filtrate in vacuo over oil of vitriol. The *potassium-salt*, obtained in like manner by decomposing the ferric salt with potash, is also a gummy mass.

*Barium-salt*, $P^4N^2H^4Ba''{}^3O^{12}$.—To prepare this salt, an alcoholic solution of chloronitride of phosphorus is decomposed by potash or ammonia; the liquid is evaporated to dryness; the residue dissolved in water; and the resulting solution of pyrophosphodiamate of potassium or ammonium is boiled with excess of barium-chloride. The pyrophosphamate of barium is then precipitated as a white granular powder, easily soluble in nitric or hydrochloric acid, insoluble in acetic acid.

The *cupric-salt*, $P^4N^2H^4Cu''{}^3O^{12}.2H^2O$ (at 100°), prepared in like manner by boiling the slightly acidulated solution of an alkaline pyrophosphodiamate with cupric sulphate, is a blue flocculent precipitate.—The *ferric salt*, $P^2NH^3Fe'''O^6$, prepared in like manner, is a white flocculent precipitate, which affords a very characteristic reaction for pyrophosphamic acid.—The *silver-salt*, $P^2NH^2Ag^3O^6$, is a white precipitate.—The *zinc-salt*, $P^4N^2H^4Zn''{}^3O^{12}$, is a white granular powder.

2. **Pyrophosphodiamic acid,** $P^2N^2H^6O^5$.—This acid is produced: 1. By the action of water, or better of alkalis, on chloronitride of phosphorus in alcoholic solution. (Gladstone.)

$$2P^3N^3Cl^6 + 15H^2O = 3P^2N^2H^6O^5 + 12HCl.$$

2. By the action of ammonia-gas on phosphoric anhydride:[*]

$$P^2O^5 + 2NH^3 = P^2N^2H^6O^5.$$

3. By passing dry ammonia-gas over phosphoric oxychloride, till it is converted into a white solid substance, taking care that the temperature does not rise too high, and treating this product with water, which dissolves it completely, the solution containing hydrochloric and pyrophosphodiamic acids, partly as ammonium-salts:

$$2(PCl^3O + NH^3) + 3H^2O = P^2N^2H^6O^5 + 6HCl.$$

The solution, when exactly neutralised with ammonia, yields precipitates of pyrophosphodiamates with several metallic salts.

The last two methods may be modified by using the very strongest solution of ammonia instead of the gas. There are also other methods of producing this acid. 4. By throwing pieces of pentachloride of phosphorus into the strongest aqueous ammonia, when some pyrophosphotriamate of ammonium is at the same time formed; but the main result accords with the following equation:—

$$2PCl^5 + 12NH^3 + 5H^2O = P^2N^2H^6O^5 + 10NH^4Cl.$$

5. By exposing phosphoric oxychloride to ammonia-gas at 100°, when 4 at. of the latter are absorbed (instead of 2 at., as described under the third method), and submitting the product to the action of water—

$$PCl^3O + 4NH^3 = PN^2H^4ClO + 2NH^4Cl.$$

$$2PN^2H^4ClO + 3H^2O = P^2N^2H^6O^5 + 2NH^4Cl.$$

6. By performing a similar experiment at a much higher temperature, the same amount of ammonia yields different products, one of which is insoluble in water, but when heated with sulphuric acid, dissolves, with the formation of pyrophosphodiamic acid.—7. The same compound is formed when pyrophosphotriamic acid is heated in a similar manner with sulphuric acid—

$$P^2N^3H^7O^4 + H^2SO^4 + H^2O = P^2N^2H^6O^5 + (NH^4)HSO^4.$$

Or, 8. When the same acid is heated alone until it begins to suffer decomposition.—9. Gerhardt's phosphamide, heated with sulphuric acid, also yields pyrophosphodiamic acid, thus—

$$2PN^2H^3O + H^2SO^4 + 3H^2O = P^2N^2H^6O^5 + (NH^4)^2SO^4.$$

The general formula of the pyrophosphodiamates is $P^2N^2H^4M^2O^5$, the acid being dibasic. It is somewhat difficult to obtain these salts pure, on account of the facility with which they are converted into pyrophosphamates.

The *barium-salt*, $P^2N^2H^4Ba''O^5$, is a gelatinous precipitate which dries up to a white earthy powder.—The *silver-salt* has the composition $P^2N^2H^4Ag^2O^5$.—The *zinc-salt*, $P^2N^2H^4Zn''O^5$, is a gelatinous precipitate easily soluble in acids, and to some extent in ammoniacal salts; when dry it forms a white powder.

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[*] Schiff (Ann. Ch. Pharm. ciii. 168), supposes that the product of this reaction is *phosphamic acid*, $PH^2NO^2$; but Gladstone has shown that it is chiefly pyrophosphodiamic acid, mixed however with metaphosphoric, and probably with other acids. (Chem. Soc. J. xvii. 229.)

**Pyrophosphotriamic acid,** $P^2N^3H^7O^4 = P^2(NH^2)^3HO^4 = \left.\begin{matrix}H^6\\(P^2O^3)^{iv}\\H\end{matrix}\right\}\begin{matrix}N^3\\O\end{matrix}$ or rather $P(NH)^3H^4O^4 = \left.\begin{matrix}H^3\\(P^2O^3)^{iv}\\H^4\end{matrix}\right\}\begin{matrix}N^3\\O\end{matrix}$.—This acid is likewise formed by the successive action of ammonia and water on phosphoric oxychloride:

$$2(PCl^3O + 4NH^3) + 2H^2O = P^2N^3H^7O^4 + 6HCl + 5NH^3.$$

When dry ammonia gas is slowly passed into a flask containing phosphoric oxychloride cooled by immersion in water, 1 at. of the oxychloride takes up 2 at. ammonia and is gradually converted, as above-mentioned, into a white solid mass. If the flask be then immersed in water at 100°, and the solid mass broken up from time to time, 2 at. more of ammonia are taken up, and on adding water to the white substance thus produced, pyrophosphotriamic acid is formed, together with pyrophosphodiamic and hydrochloric acids, the two latter dissolving, while the former remains behind, and may be purified by washing, first with cold water, then with a little dilute alcohol.

Pyrophosphotriamic acid thus obtained is a white, amorphous, tasteless powder, which reddens litmus when moistened. It is nearly insoluble in water, but is very slowly attacked by it at ordinary temperatures, more quickly when heated, yielding pyrophosphodiamic acid:

$$P^2N^3H^7O^4 + H^2O = P^2N^2H^6O^5 + NH^3.$$

When boiled with hydrochloric acid, it is speedily resolved into phosphoric acid and ammonia, pyrophosphodiamic acid being an intermediate product.

Pyrophosphotriamates.—The acid, as already observed, is tetrabasic, the general formula of its normal salts being most probably $P^2(NH)^3M^4O^4$ or $\left.\begin{matrix}H^3\\(P^2O^3)^{iv}\\M^4\end{matrix}\right\}\begin{matrix}N^3\\O\end{matrix}$. The acid effervesces with solutions of alkaline carbonates, and when suspended in solutions of metallic salts, usually decomposes them, even in presence of the liberated acid. All the pyrophosphotriamates, even those of the alkali-metals, are insoluble or sparingly soluble in water.

The *ammonium-salt*, $P^2N^3H^6(NH^4)O^4$, formed by decomposing carbonate of ammonium with the acid, cakes together in small white lumps, and readily gives up its ammonia to dilute acids even in the cold.

*Barium-salts.* The *monobarytic salt*, $P^4N^6H\ ^2Ba''O^8$, is prepared by diffusing the acid through a solution of barium-chloride, and carefully neutralising the liberated acid with ammonia. The *dibarytic salt*, $P^4N^6H^{10}\overset{''}{Ba}{}^2O^8$ or $P^2N^3H^5Ba''O^4$, by suspending the acid in excess of an ammoniacal solution of barium-chloride.

A white *cadmium-salt* is obtained by treating the acid with chloride of cadmium; a green *chromium-salt*, with chromic acetate. The *cobalt-salt*, $P^2N^3H^5Co''O^4$, produced by digesting the acid with a slightly ammoniacal solution of cobalt-nitrate, has a beautiful violet colour: it is not decomposed by hydrochloric acid, and but slowly by dilute sulphuric acid.

*Copper-salts.* The *monocupric salt*, $P^4N^6H^{12}Cu''O^8$, is obtained as a pale blue compound (not quite pure) by treating the acid with a slightly acidulated solution of cupric nitrate. The *dicupric salt*, $P^4N^6H^{10}\overset{''}{Cu}{}^2O^8$, obtained by digesting the acid with cupric acetate, is greenish.

*Iron-salt.* A *monoferrous salt*, $P^4N^6H^{12}Fe''O^8$, produced by digesting the acid with ferrous sulphate, has a yellow-drab colour, and is insoluble in dilute acids. No *ferric* pyrophosphotriamate has yet been obtained.

*Lead-salts.*—The *monoplumbic salt*, $P^4N^6H^{12}Pb''O^8$, is obtained pure by digesting the acid with a decidedly acid solution of plumbic nitrate; the *diplumbic salt*, $P^4N^6H^{10}\overset{''}{Pb}{}^2O^8$, by using a solution only slightly acidulated; the *triplumbic salt*, $P^4N^6H^6\overset{''}{Pb}{}^3O^8$, by warming the acid with basic acetate of lead.

*Magnesium-salts.*—The product obtained by warming the acid with an ammoniacal solution of magnesia, washing with water containing a little ammonia, and afterwards with pure water, appears to be a mixture of mono- and di-magnesic pyrophosphotriamates.

The *manganese-salt* is yellowish.

*Mercury-salt*, $P^2N^3H^3\overset{''}{Hg}{}^2O^4$, obtained by diffusing the acid through a solution of mercuric chloride, or a slightly acidulated solution of ammonio-mercuric chloride, is a heavy, white, granular powder which becomes yellowish, and eventually dark-coloured on exposure to light. Iodide of potassium first turns it scarlet, and then dissolves out the mercury.

*Nickel-salt.*—A feebly ammoniacal solution of nickel-sulphate yields a bright green pyrophosphotriamate.

*Platinum-salt*, $P^2N^3H^3Pt^{iv}O^4$.—Obtained by treating the acid with a strong solution of platinic chloride, as a bulky yellowish compound, which must be washed with alcohol, as water decomposes it in presence of the liberated acid.

*Potassium-salt*, $P^2N^3H^6KO^4$.—White, almost insoluble salt, produced by decomposing carbonate of potassium with pyrophosphotriamic acid. It is easily decomposed by acids.

*Silver-salts.*—The *mono-argentic salt*, $P^2N^3H^6AgO^4$, is obtained as a white flocculent precipitate, soon becoming granular, by adding nitrate of silver to water in which the acid is suspended, and may be purified by digestion in dilute nitric acid or ammonia, which dissolves out a slight excess of silver. It is insoluble in water, and is completely decomposed by hydrochloric acid.—The *triargentic salt*, $P^2N^3H^4Ag^3O^4$, is obtained by precipitating an ammoniacal solution of silver-nitrate with a solution of pyrophosphotriamic acid, or better, by treating the mono-argentic-salt with ammoniacal silver-nitrate. It is of a bright yellow colour, heavy, granular, and when dry forms an orange-yellow powder. Dilute nitric acid or ammonia converts it into the mono-argentic salt. Acetic acid attacks it but slowly.

*Thallium-salt.*—The acid treated with nitrate of thallium forms a heavy white compound, easily decomposed by rather strong nitric acid.

*Zinc-salt.*—The acid decomposes chloride of zinc, forming a white pyrophosphotriamate.

**PYROPHOSPHORIC ACID.** See Phosphorus, Oxygen-acids of (p. 539).

**PYROPHYLLITE.** A hydrated aluminic silicate occurring in foliated, talc-like, subtransparent masses, having a white, green, or yellow colour and pearly lustre; hardness = 1; specific gravity = 2·7—2·8; flexible in thin laminæ. Before the blowpipe it swells up, without fusing, in fan-like shapes, increasing to about twenty times its original bulk. It forms a clear yellow glass with soda, and gives a fine blue colour with cobalt-solution. Partially soluble in sulphuric acid.

*Analyses.*—*a.* From Pschminsk in the Ural (Hermann, Pogg. Ann. xv. 392).—*b.* Spa in Belgium (Rammelsberg, *ibid.* lxviii. 513).—*c.* Westana in Sweden (Berlin, *ibid.* lxxviii. 414).—*d.* Chesterfield County, South Carolina (Genth, Sill. Am. J. [2] xviii. 449):

| | $SiO^2$. | $Al^2O^3$. | $Fe^2O^3$. | MnO. | MgO. | CaO. | $H^2O$. | | |
|---|---|---|---|---|---|---|---|---|---|
| *a.* | 59·79 | 29·46 | 1·80 | . . | 4·00 | . . | 5·62 | = | 100·67 |
| *b.* | 66·14 | 25·87 | . . | . . | 1·49 | 0·39 | 5·59 | = | 99·48 |
| *c.* | 66·69 | 25·63 | 0·76 | 0·29 | 0·17 | 0·67 | 6·45 | = | 100·66 |
| *d.* | 65·41 | 28·50 | 0·91 | . . | 0·25 | 0·39 | 5·23 | = | 100·69 |

The last three analyses may be represented approximately by the formula $2Al^2O^3.9SiO^2.3H^2O$; the first by $(Mg''O.SiO^2).3(Al^2O^3.3SiO^2).3H^2O$. Some of the Chinese agalmatolites (i. 60) approach very nearly to pyrophyllite. (Rammelsberg's *Mineralchemie*, p. 586.)

**PYROPHYSALITE.** Syn. with Physalite (p. 634).

**PYROPIN.** The name given by Thomson (Phil. Mag. xviii. 372) to a red substance extracted from elephants' teeth; apparently an albuminoïd.

**PYROPISSITE.** A yellowish-brown, opaque, earthy substance, occurring in the lignite of Weissenfels. Boiling alcohol extracts from it 30 per cent. of a white, fusible, combustible matter. When heated above 100° it melts with tumefaction, and evolution of white vapours, to a black inflammable mass; soluble for the most part in oil of turpentine. By distillation, according to Marchand, it yields 62 per cent. paraffin, and 3 cubic feet of illuminating gas, from a pound of the material. (Kenngott, Min. Forsch. 1850—51, p. 148.)

**PYROQUINOL.** Syn. with Hydroquinone (iii. 213).

**PYRORACEMIC ACID.** $C^3H^4O^3 = \left.\begin{matrix}C^3H^3O^2\\H\end{matrix}\right\}O$. *Pyruvic acid. Brenztraubensäure.* (Berzelius Ann. Ch. Pharm. xiii. 61.—Völckel, *ibid.* lxxxix. 65. Wislicenus, *ibid.* cxxvi. 225.)—An acid homologous with glyoxalic acid ($C^2H^2O^3$) produced by the dry distillation of racemic or tartaric acid: probably thus:

$$C^4H^6O^6 = C^3H^4O^3 + CO^2 + H^2O.$$

To prepare it, tartaric acid is distilled at a temperature gradually rising to 300°, and the distillate is redistilled several times, the portion which goes over between 165° and 170° being ultimately collected apart. This distillate left for some days over oil of vitriol and solid potash, yields pure pyroracemic acid. (Völckel.)

Pyroracemic acid is a liquid having a faint yellowish colour, smelling like acetic acid, and boiling at about 165°, but with partial decomposition at each distillation. It is soluble in water, alcohol, and ether.

When subjected in aqueous solution to the action of *nascent hydrogen*—evolved by sodium-amalgam (Wislicenus), or by zinc and sulphuric acid (Debus)—or of *hydriodic acid*, or *iodide of phosphorus*, it takes up 2 at. hydrogen, and is converted into lactic acid $C^3H^6O^3$, or if the reducing agent is employed in larger excess, into propionic acid (p. 730). It unites directly with 2 at. *bromine*, forming the compound $C^3H^4Br^2O^3$, probably bromolactic acid. These reactions show that pyroracemic acid is related to lactic acid in the same manner as acrylic to propionic acid, also that its relation to acrylic acid is the same as that of lactic to propionic acid. (Wislicenus.)

Pyroracemates. The acid is monobasic, the formula of its salts being $C^3H^3MO^3$. They crystallise well, provided that heat is avoided in their preparation. The *potassium-* and *sodium-salts* are deliquescent. The *sodium-salt* forms large anhydrous prisms, $C^3H^3NaO^3$. The *lead-salt*, $C^6H^6Pb''O^6$, is a crystalline precipitate. The *silver-salt* is also crystalline, and may be recrystallised from boiling water.

*β.-Pyroracemic acid.*—When an aqueous solution of pyroracemic acid is evaporated by heat, there remains a non-volatile syrupy mass which appears to be a polymeric modification of the acid. It is likewise produced when the acid is separated from its salts This syrupy acid does not form crystallisable salts, its salts being all amorphous and gummy. The same gummy salts are obtained when the solutions of the crystalline pyroracemates are evaporated by heat.

When pyroracemic is treated with excess of baryta, a yellowish precipitate is formed having the composition of a basic barium-salt of tripyroracemic acid, $C^{18}H^{18}Ba''^3O^{18}.Ba''H^2O^2$. On boiling this precipitate for some hours with excess of barytic hydrate, oxalate of barium separates out, and the supernatant liquid, when freed from baryta by sulphuric acid and evaporated, leaves a syrup which partly solidifies in the crystalline form (Finck, Ann. Ch. Pharm. cxxii. 182). The crystals when purified by recrystallisation from alcohol and ether, constitute Finck's uvitic acid, $C^9H^8O^4$, which melts at 287°, sublimes without decomposition, and forms crystallisable salts, the sparingly soluble silver-salt having the composition $C^9H^6Ag^2O^4$.—The syrupy liquid, Finck's uvitonic acid, has, according to his analysis, the composition $C^9H^{12}O^7$. It forms amorphous salts, and appears, both from its properties and from the analysis, to be merely the above-mentioned syrupy modification of pyroracemic acid. (Kekulé, *Lehrbuch*, ii. 213.)

**PYRORETIN.** Retinite from the lignite of Aussig in Bohemia (see RETINITE).

**PYRORTHITE.** See ORTHITE (p. 237).

**PYROSCLERITE,** including *Kæmmererite.*—These minerals are alumino-silicates containing chromium. They occur in six-sided prisms, apparently belonging to the hexagonal system, with perfect basal cleavage; also massive.

*Pyrosclerite* is translucent, with a green-greyish or reddish colour, and weak pearly lustre. Hardness = 2·5—3. Specific gravity = 2·6—2·74. Fracture uneven and splintery. Gives off all its water at a strong heat; melts with difficulty before the blowpipe to a grey glass, and gives with fluxes a faint chrome reaction. Decomposed by hydrochloric acid.

*Kæmmererite* is also translucent and has a pearly lustre; but its colour is reddish-violet like that of lepidolite. Hardness = 1·5—2. Specific gravity = 2·617—2·62. Sectile and flexible. Feels greasy. Gives off empyreumatic water when heated. Exfoliates slightly before the blowpipe, but does not fuse; gives with fluxes the reactions of chromium. Decomposed by hydrochloric acid.

*Rhodochrome* is a variety of kæmmererite, having a greenish-black colour in the mass, but peach-blossom red in thin splinters. Hardness = 2·5—3. Specific gravity = 2·65—2·67. When strongly heated before the blowpipe, it melts on the edges to a yellow enamel.

*Analyses.*—*a.* Pryrosclerite from Elba (v. Kobell, J. pr. Chem. ii 51).—*b.* Kæmmererite from Bissersk in Siberia (Hartwall, Berz. Jahresb. xxiii. 266).—*c.* K. from Lake Atkall in the Urals *α.* crystallised; *β.* massive: *rhodochrome* (Hermann, J. pr. Chem. liii. 22).—*d.* K. from Texas, Lancaster County, Pennsylvania: *α.* by Genth (Sill. Am. J. [2] xv. 438); *β.* by Smith and Brush (*ibid.* xvi. 41).

| | Pyrosclerite. | Kæmmererite. | | | | |
|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | | *d.* | |
| | | | α. | β. | α. | β. |
| Silica. . . | 37·03 | 37·0 | 30·58 | 34·64 | 32·98 | 33·28 |
| Alumina . . | 13·50 | 14·2 | 15·94 | 10·50 | 11·11 | 10·60 |
| Chromic oxide . | 1·43 | 1·0 | 4·99 | 5·50 | 6·85 | 4·72 |
| Magnesia . . | 31·62 | 31·5 | 33·45 | 35·47 | 35·22 | 36·00 |
| Lime . . . | . . | 1·5 | . . | . . | 0·38 | 0·35 |
| Ferrous oxide . | 3·52 | 1·5 | 3·32 | 1·80 | 1·29 | 1·60 |
| Water . . | 11·00 | 13·0 | 12·05 | 12·03 | 13·12 | 12·95 |
| | 98·10 | 99·7 | 100·33 | 99·94 | 100·95 | 99·50 |

All these minerals may be represented as compounds of a metasilicate, $\mathrm{M''SiO^3}$ or $\mathrm{M''O.SiO^2}$ with an aluminate, $\mathrm{\overset{''}{M}{}^3\overset{'''}{Al}{}^2O^6}$ or $\mathrm{3M''O.\overset{'''}{Al}{}^2O^3}$, and water, the aluminium being partly replaced by chromium, and to a greater extent in kæmmererite than in pyrosclerite. Calling the silicate A and the aluminate B,

*a.* may be represented as 9 *A* + *B* + 9 aq.
*b.* „ 9 *A* + *B* + 12 aq.
*c, d.* „ 6 *A* + *B* + 9 aq.

*Vermiculite* from Milbury, Massachusetts, may be regarded as belonging to the same family, though it contains no chromium. It has a granular, scaly structure, and greasy feel, and is especially characterised by its behaviour before the blowpipe, opening out into wormlike threads, expanding to many times its original bulk, and ultimately melting to a yellowish-green glass. It is decomposed by hydrochloric acid. Contains, according to Crossley (*Dana's Mineralogy*, ii. 292), 35·74 per cent. $\mathrm{SiO^2}$, 16·42 $\mathrm{Al^2O^3}$, 27·44 MgO, 10·92 FeO and 10·30 water, and may be represented by the formula $\mathrm{8M''SiO^3.\overset{''}{M}{}^3\overset{'''}{Al}{}^2O^6}$. 8 aq.

*Chonicrite* (i. 931), *Loganite* (iii, 732), and *Tabergite* are sometimes also classed with pyrosclerite.

**PYROSMALITE.** A silicate of iron and manganese containing chlorine, occurring in hexagonal prisms or tables having the principal axis = 0·5307, and exhibiting the faces oP, P, 2P, ∞P Cleavage perfect parallel to the base, imperfect parallel to ∞P. It also occurs massive. Hardness = 4—4·5. Specific gravity = 3·0—3·2. It has a brown colour and pearly lustre; streak paler than the colour. Fracture uneven, rather splintery; somewhat brittle. When strongly heated before the blowpipe it melts to a black slag, attractable by the magnet. Fuses readily with borax, exhibiting the reactions of iron and manganese. Dissolves perfectly in strong nitric acid.

A specimen from the Bjelkey mine near Nordmarken in Wermland, Sweden, was found by Hisinger (Schw. J. xiii. 341; xxiii. 54) to contain 35·85 per cent. $\mathrm{SiO^2}$, 35·48 $\mathrm{Al^2O^3}$, 24·26 $\mathrm{Mn^2O^3}$, 1·21 CaO, 3·77 chlorine, and a quantity of water not determined. Its composition may be represented approximately by the formula $\mathrm{\overset{'''}{Fe}{}^2Cl^6.3(4M''O.3SiO^2 + 2\ aq.)}$.

Pyrosmalite occurs also at Nya Kopparberg in Westmannland.

**PYROSORBIC ACID.** Syn. with Maleic Acid.

**PYROSTEARIN.** The name applied by Berzelius to the less fusible portion of the distillate obtained by distilling empyreumatic oils with water, the more fusible portion being called *pyrelaïn* (Handw. d. Chem. 2te. Aufl. ii. [2] 418).

**PYROSTIBITE.** Syn. with Kermesite or Red Antimony (iii. 446).

**PYROTARTARIC ACID.** $\mathrm{C^5H^8O^4} = \left.\begin{matrix}\mathrm{(C^5H^6O^2)''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}$.—This acid was discovered in 1807 by Valentin Rose, among the products of the distillation of tartar. It has been investigated chiefly by Gruver (Trommsd. N. J. xxiv. 2, 55), Pelouze (Ann. Ch. Phys. [2] lvi. 297), Weniselos (Ann. Ch. Pharm. xv. 148), Arppe (*ibid.* lxvi. 73), and Kekulé (*ibid.* Suppl. i. 342).

It is produced—1. By the dry distillation of tartaric acid:

$$\mathrm{2C^4H^6O^6 = C^5H^8O^4 + 3CO^2 + 2H^2O};$$

2. By the action of sodium-amalgam on itaconic acid or its isomers, citraconic or mesaconic acid:

$$\underset{\text{Itaconic acid.}}{\mathrm{C^5H^6O^4}} + \mathrm{Hg''Na^2} = \mathrm{Hg} + \underset{\text{Pyrotartrate of sodium.}}{\mathrm{C^5H^6Na^2O^4}}.$$

This reaction is analogous to that by which the homologous body fumaric acid, $\mathrm{C^4H^4O^4}$ is converted into succinic acid (ii. 743).

It may also be formed from itaconic acid by converting the latter into dibromopyrotartaric acid, and reducing the latter with sodium-amalgam. (**Kekulé.**)

3. By heating cyanide of tritylene with alcoholic potash, the action being analogous to that by which the fatty acids are formed from the cyanides of the monatomic radicles $C^nH^{2n+1}$ (**Maxwell Simpson**):

$$C^3H^6(CN)^2 + 4H^2O = 2NH^3 + C^5H^8O^4.$$

*Preparation.*—1. From **Tartaric acid.** Tartaric mixed with an equal weight of pounded pumice is distilled in a capacious retort; the distillate is diluted with water; the empyreumatic oil is removed by filtration; the filtrate is evaporated to the crystallising point; and the crystals are freed from adhering oil by spreading them out on paper under a bell-jar near a dish containing alcohol. This process yields a quantity of pyrotartaric acid equal to 7 per cent. of the tartaric acid used.

2. From **Itaconic acid.** Sodium-amalgam is added to aqueous itaconic acid, and the liquid, decanted from the separated mercury, is saturated with hydrochloric acid and evaporated: the residue is treated with alcohol, which dissolves out the pyrotartaric acid and leaves the greater part of the chloride of sodium; the alcoholic solution is evaporated to dryness; and the pyrotartaric acid is extracted from the residue by ether. (**Kekulé.**)

*Properties.*—Pyrotartaric acid crystallises in colourless, sometimes well developed prisms with rhombic base and truncated on the lateral edges. It is very soluble in water, alcohol and ether: 1 pt. of it dissolves in 1½ pt. water at 20°. It melts at 112°, begins to boil at about 200° and then volatilises, being partly converted into pyrotartaric anhydride $C^5H^6O^3$. It is not attacked by nitric acid or by cold sulphuric acid.

A concentrated aqueous solution of pyrotartaric acid does not produce any turbidity in baryta- strontia- or lime-water, or in solution of nitrate or neutral acetate of lead; but with basic acetate of lead it forms a copious white curdy precipitate insoluble in water, but very soluble in the basic lead-acetate and in excess of acid.

**Pyrotartrates.** Pyrotartaric acid is dibasic, forming neutral and acid salts, the general formulæ of which are:

| | Neutral. | Acid. |
|---|---|---|
| For monatomic metals . | $C^5H^6M^2O^4$ | $C^5H^7MO^4$ |
| For diatomic metals . | $C^5H^6M''O^4$ | $C^{10}H^{14}M''O^8$ or $C^5H^6M''O^4.C^5H^8O^4$. |

There are also a few basic pyrotartrates of di- and triatomic metals. The acid salts of the alkali-metals and alkaline-earth-metals, obtained by neutralising a certain quantity of pyrotartaric acid with the base and then adding a quantity of the acid equal to the former, crystallise well; the soluble neutral salts are somewhat difficult to crystallise.

***Pyrotartrates of Aluminium.*** Moist hydrate of aluminium dissolves easily in pyrotartaric acid, and the solution when concentrated yields crystals. A *basic salt*, $2C^5H^6O^4.Al^2O^3$ or $2(C^{15}H^{21}Al'''O^{12}.Al^2O^3).3H^2O$, is obtained as a heavy powder by precipitating a neutral solution of aluminic chloride with neutral pyrotartrate of sodium, or by boiling moist alumina with a quantity of the acid not sufficient to dissolve it.

***Ammonium-salts.***—The *neutral salt* is deliquescent, and gives off ammonia on evaporation. The *acid salt*, $C^5H^7(NH^4)O^4$, forms beautiful rhomboïdal prisms, permanent in the air, very soluble in water.

***Barium-salts.***—The *neutral salt*, $C^5H^6Ba''O^4.2H^2O$, is a crystalline powder formed of small rhomboïdal prisms, very soluble in water, insoluble in alcohol.—The *acid salt*, $C^{10}H^{14}Ba''O^8.2H^2O$, forms stellate groups of crystals.

***Bismuth-salt.***—A solution of recently precipitated bismuth-hydrate in pyrotartaric acid yields on addition of water, a precipitate containing $C^{15}H^{12}Bi'''^4O^{12}.5H^2O$.

***Cadmium-salts.***—*a. Neutral*, $C^5H^6Cd''O^4.3H^2O$.—The solution of cadmic carbonate in the aqueous acid yields, by concentration, crystalline grains very soluble in water, insoluble in alcohol, and still retaining 1 at. water at 200°.—*β.* The *acid salt* is obtained by evaporation as a viscous mass in which a few long needles form after a while.

***Calcium-salts.***—*a. Neutral*, $C^5H^6Ca''O^4.2H^2O$.—White pulverulent precipitate, slightly soluble in water, very soluble in acetic, hydrochloric, and nitric acids, insoluble in alcohol.—*β.* The *acid salt*, obtained by evaporating a solution of the neutral salt in pyrotartaric acid, forms crystals containing $C^5H^6Ca''O^4.5C^5H^8O^4.2H^2O$. (**Arppe.**)

***Cobalt-salt.***—The solution of cobalt-hydrate in pyrotartaric acid deposits on evaporation colourless crystals of the acid mixed with a red insoluble salt. On neutralising the acid liquid with ammonia, a rose-coloured crystalline powder is formed, which dissolves in water, but is decomposed at the same time.

*Copper-salts.*—α. *Neutral*, $C^5H^6Cu''O^4.2H^2O$.—Pyrotartrate of sodium forms with cupric salts a blue precipitate soluble in about 250 pts. of water, very soluble in acids and ammonia; it retains 1 at. water at 100°.—β. A *basic salt*, $C^5H^6Cu''O^4Cu''H^4O^2$, is deposited in greenish flocks on evaporating a solution of the neutral salt in ammonia, after addition of water.

*Glucinum-salts.*—Pyrotartaric acid saturated with glucina leaves when evaporated over oil of vitriol, a crystalline acid salt, $C^5H^6G''O^4.C^5H^8O^4$, which when heated to 180° is converted into the neutral salt, $C^5H^6G''O^4$.

*Iron-salts.*—α. *Ferrous salt.*—The acid dissolves iron, with evolution of hydrogen, forming a solution which quickly turns red, and deposits red flocks on addition of water or alcohol.—β. *Ferric salt.* Ferric chloride forms with pyrotartrate of sodium a red viscous precipitate containing $2C^5H^8O^4.Fe^2O^3.3H^2O$ or $C^{15}H^{21}Fe'''O^{12}.Fe^2O^3.6H^2O$.

*Lead-salt*, $C^5H^6Pb''O^4.2H^2O$.—Precipitated after a few hours from a solution of the potassium-salt mixed with nitrate or neutral acetate of lead, in needles if the solution contains free acid, as a powder if it is neutral. It dissolves in small quantity in boiling water, and is deposited in needles on cooling: dissolves also in nitrate of lead. The same salt is formed by treating carbonate of lead with pyrotartaric acid and filtering to separate a basic salt. Pyrotartaric acid forms a curdy precipitate with basic acetate of lead (p. 772).

*Magnesium-salts.*—A solution of magnesia in pyrotartaric acid evaporated over oil of vitriol, leaves the neutral salt as a gummy very friable mass, apparently containing $C^5H^6Mg''O^4.3H^2O$. The same solution evaporated to a syrup, and then mixed with water, deposits a crystalline mass consisting of $C^5H^6Mg''O^4.6H^2O$.—The *acid salt* is gummy.

The *manganese-salt*, $C^5H^6Mn''O^4.3H^2O$, is obtained by evaporation as a gummy mass, very soluble in water, insoluble in alcohol.

The *mercurous* and *mercuric salts* are white precipitates.

*Nickel-salts.*—The *neutral salt*, $C^5H^6Ni''O^4.2H^2O$, is obtained by evaporating the green solution of nickel-hydrate in the acid, redissolving in alcohol, and again evaporating, as a green, crystalline, sparingly soluble powder, which gives off its water at 200°. —The *acid salt*, $C^5H^6Ni''O^4.C^5H^8O^4.H^2O$, is obtained as a crystalline mass by leaving the solution of the hydrate in pyrotartaric acid to evaporate over oil of vitriol.

*Potassium-salts.*—The *neutral salt*, $C^5H^6K^2O^4.H^2O$, is very soluble, deliquescent, and may with some difficulty be obtained in foliated crystals by evaporating its solution in a hot air chamber.—The *acid salt*, $C^5H^7KO^4$, is obtained by spontaneous evaporation of a solution of the acid half saturated with potash, in colourless, oblique, rhomboïdal prisms, permanent in the air.

The *silver-salt*, $C^5H^6Ag^2O^4$, is a white, curdy precipitate which blackens when exposed to light. By heating it in a current of dry hydrogen, and washing the product with water to remove free acid, a brown powder is obtained consisting of *argentous pyrotartrate*.

*Sodium-salts.*—The *neutral salt*, $C^5H^6Na^2O^4.6H^2O$, forms efflorescent laminæ very soluble in water, insoluble in alcohol.—The *acid salt*, $C^5H^7NaO^4$, crystallises with difficulty in small rhomboïdal prisms.

*Strontium salts.*—The *neutral salt*, $C^5H^6Sr''O^4.H^2O$, forms prisms very soluble in water, insoluble in alcohol.—The *acid salt*, $C^5H^6Sr''O^4.C^5H^8O^4.2H^2O$, crystallises in nacreous scales.

*Tin-salt.*—Stannous oxide dissolves easily in pyrotartaric acid, and the solution, filtered from a yellow basic salt, yields with alcohol a precipitate apparently containing $C^5H^6Sn''O^4.Sn''O$.

*Uranic salt.*—The yellow solution of uranic hydrate in the acid deposits on evaporation, a yellow powder, very soluble in water, insoluble in alcohol, and containing according to Arppe, $C^{15}H^{21}U''O^{12}.\overset{'''}{U}{}^3H^3O^6$ or $2C^5H^6(U^2O^2)''O^4.C^5H^8O^4.2H^2O$.

*Zinc-salts.*—The *neutral salt*, $C^5H^6Zn''O^4.3H^2O$, is obtained by evaporation as a thick syrup, gradually depositing crystalline granules which increase in quantity on addition of a small quantity of water. It retains 1 at. water at 200°.—An insoluble *basic salt* is obtained by concentrating a solution of zinc in pyrotartaric acid to a small bulk and treating the residue with water.

**Dibromopyrotartaric acid,** $C^5H^6Br^2O^4$.—This compound has not yet been obtained as a substitution-product of pyrotartaric acid, but is formed by direct addition of bromine to itaconic acid, $C^5H^6O^4$. To prepare it, 4 pts. of itaconic acid are shaken up with 5 pts. of bromine and 4 or 5 pts. of water. The reaction commences at ordinary temperatures and is attended with evolution of heat, but towards the end it must be assisted by the heat of a water-bath. The crystalline crust which separates on cooling, and the crystals obtained by evaporating the mother-liquor, are purified by recrystallisation from a small quantity of water.

Dibromopyrotartaric acid forms colourless crystals easily soluble in water, alcohol, and ether. When treated with *sodium-amalgam*, it is converted into pyrotartaric acid. On adding oxide of silver to the aqueous solution, the 2 at. bromine are replaced by 2 at. HO, and an acid, $C^5H^8O^6$, homologous with tartaric acid, is produced:

$$C^5H^6Br^2O^4 + Ag^2O + H^2O = 2AgBr + C^5H^8O^6.$$

Dibromopyrotartaric acid is dibasic. Its salts have not been much examined. In preparing them it is necessary to avoid rise of temperature, as they are easily decomposed thereby, with separation of metallic bromide and formation of a crystallisable monobasic acid, called aconic acid, $C^5H^4O^4$; *e.g.:*

$$C^5H^4Br^2Na^2O^4 = 2NaBr + C^5H^4O^4.$$

On boiling a solution of the sodium-salt and adding carbonate of sodium in such quantity, that 3 at. sodium shall be present for every 1 at. of dibromopyrotartaric acid, a solution is obtained which on sufficient concentration, yields large crystalline plates of aconate of sodium, obtainable by slow evaporation from aqueous solution, in large, well-developed, efflorescent crystals containing $C^5H^3NaO^4.3H^2O$. In like manner by boiling a solution of barytic dibromo-pyrotartrate, adding carbonate of barium in sufficient quantity to neutralise the reaction, and mixing the filtrate with alcohol, aconate of barium, $C^{10}H^6Ba''O^8$, is precipitated in white flocks, very soluble in water, insoluble in strong alcohol, crystallising in needles from dilute alcohol.

By treating citraconic and mesaconic acids which are isomeric with itaconic acid, with bromine and water as above, acids are produced, isomeric but not identical with the dibromopyrotartaric acid just described. The three isomeric acids may be distinguished as ita-, citra-, and mesa-dibromopyrotartaric acids.

*Citra-dibromopyrotartaric acid*, $C^5H^6Br^2O^4$, is much more soluble than ita-dibromopyrotartaric acid. It usually crystallises in cauliflower-like groups of microscopic needles. When heated it yields monobromocitraconic anhydride, $C^5H^3BrO^3$:

$$C^5H^6Br^2O^4 = C^5H^3BrO^3 + H^2O + HBr.$$

Citra-dibromopyrotartaric acid is also dibasic, and its salts are readily decomposed by boiling with water or excess of base, but in a totally different manner from the ita-dibromopyrotartrates, carbonic anhydride being given off, and a salt of monobromocrotonic acid produced: thus,

$$\underset{\substack{\text{Citra-dibromopyro-}\\\text{tartrate of sodium.}}}{C^5H^4Br^2Na^2O^4} = \underset{\substack{\text{Monobromocrotonate}\\\text{of sodium.}}}{C^4H^4BrNaO^2} + NaBr + CO^2.$$

$$\underset{\substack{\text{Citro-dibromopyro-}\\\text{tartrate of calcium.}}}{2C^5H^4Br^2Ca''O^4} = \underset{\substack{\text{Monobromocrotonate}\\\text{of calcium.}}}{C^8H^8Br^2Ca''O^4} + Ca''Br^2 + 2CO^2.$$

(See CROTONIC ACID in the APPENDIX.) According to Cahours (Ann. Ch. Phys. [3] lxvii. 137), an acid having the composition of dibromobutyric acid is formed at the same time as an intermediate product:

$$C^5H^6Br^2O^4 = C^4H^6Br^2O^2 + CO^2.$$

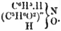
*Mesa-dibromopyrotartaric acid* is much less soluble than citra-, but more soluble than ita-dibromopyrotartaric acid. It crystallises in nodular or spherical masses. Its salts when boiled with water likewise yield bromocrotonic acid. (Kekulé, Ann. Ch. Pharm. Suppl. ii. 100.)

**PYROTARTARIC ANHYDRIDE.** $C^5H^6O^3 = C^5H^6O^2.O.$—Obtained by distilling the acid with phosphoric anhydride. It is a liquid boiling at a temperature above 300°, insoluble in water, but gradually converted by absorption of water into pyrotartaric acid.

**PYROTARTARIC ETHERS.** The only one known is the *ethylic ether*, $C^5H^6(C^2H^5)^2O^4$, which is produced by passing hydrochloric acid gas into an alcoholic solution of the acid. It is an aromatic liquid boiling at 218°, gradually decomposed by water.

**PYROTARTRANIL,** or *Phenyl-pyrotartrimide*, $C^{11}H^{11}NO^2 = \left.\begin{matrix}(C^5H^6O^2)''\\C^6H^5\end{matrix}\right\}N.$ (Arppe, Ann. Ch. Pharm. xc. 138.)—Produced by heating aniline with pyrotartaric acid to a temperature a little above 100° for about ten minutes. On dissolving the solidified mass in boiling water, treating the solution with animal charcoal, and leaving it to cool, pyrotartranil is deposited as a pulverulent precipitate composed of microscopic needles. It has neither taste nor smell; melts at 98°, sublimes without decomposition at 140°, boils with partial decomposition at about 300°. It is slightly soluble in boiling *water*, easily soluble in *alcohol* and *ether*, also in *aqueous alkalis*, by which when heated it is converted into pyrotartranilic acid. When fused with *alkaline hydrates*, it is resolved into aniline and pyrotartaric acid. *Nitric acid* converts it into pyrotartronitranil.

**PYROTARTRANILIC ACID,** or *Phenyl-pyrotartramic acid*, $C^{11}H^{13}NO^3$ =



$\left.\begin{matrix}C^6H^5.H\\(C^5H^6O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Arppe, *loc. cit.*)—Produced by the action of aniline on pyrotartaric anhydride; also by the metamorphosis of pyrotartranil under the influence of aqueous alkalis. It forms bulky needles, appearing under the microscope as rectangular prisms with perpendicular end-faces. It is more soluble in *water* than pyrotartranil, easily soluble in *alcohol* and *ether;* reddens litmus. It may be heated to 140° without loss of weight, but at 147° it gives off water and is converted into pyrotartronitranil. It is decomposed by excess of boiling *potash;* is not coloured by chloride of lime.

Pyrotartranilic acid decomposes carbonates, but is separated from its own salts by acetic acid. The pyrotartranilates of the alkali- and alkaline-earth metals are very soluble in water. The *ammonium-salt*, which may be obtained by boiling pyrotartranil with aqueous ammonia, dries up to a radiate mass very soluble in cold but decomposed by hot water. Its solution forms a bluish-green precipitate with *cupric sulphate*, white with *mercuric chloride*, yellowish-red with *ferric chloride*. The *lead-salt*, $C^{16}H^{14}Pb''(C^6H^5)^2N^2O^6$, forms a white precipitate becoming glutinous on ebullition.

**PYROTARTRIMIDE,** $C^5H^7NO^2$ =

$\left.\begin{matrix}(C^5H^6O^2)''\\H\end{matrix}\right\}N$, or *Dipyrotartro-diamide*,

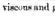
$\left.\begin{matrix}(C^5H^6O^2)^2\\H^2\end{matrix}\right\}N^2$. (Arppe, Ann. Ch. Pharm. lxxxvii. 228.)—Produced by heating acid pyrotartrate of ammonium:

$$C^5H^7(NH^4)O^4 - 2H^2O = C^5H^7NO^2.$$

The solidified distillate is purified by pressure and recrystallisation from a small quantity of water.

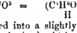
Pyrotartrimide forms small needles or hexagonal plates, belonging to the trimetric system, and exhibiting the combination $oP . \infty\bar{P}\infty . \infty P$. Angle $\infty P : \infty P = 92° 30'$; $\infty P : \infty\bar{P}\infty = 133°$. Cleavage parallel to $\infty P$ and $oP$. It is anhydrous, very soluble in water, alcohol, ether, acids and alkalis; has a cooling, slightly bitter, and sour taste; its aqueous solution reddens litmus, but it does not combine with ammonia. It melts at 66°, and solidifies on cooling, in a radiate mass, unctuous to the touch, and having a foliated fracture. It begins to volatilise at 100°, but does not boil till heated to about 280°, at which temperature it suffers partial decomposition. When boiled with strong *potash-ley*, it gives off ammonia. Its solution forms with *oxide of lead*, a strongly alkaline compound which contains 67·23 per cent. PbO and 5·47 water, dries up to a gummy mass, and is partly decomposed by water. The solution of this lead-compound attacks the paper through which it is filtered, rendering it viscous and gelatinous.

**PYROTARTRONITRANIL,** $C^{11}H^{10}N^2O^4$ or *Nitrophenyl-pyrotartrimide* =



$\left.\begin{matrix}(C^5H^6O^2)''\\C^6H^4(NO^2)\end{matrix}\right\}N$. (Arppe, *loc. cit.*).—Precipitated by water from a solution of pyrotartranil in very strong nitric acid, as an oil which gradually solidifies, and crystallises from boiling alcohol in spherical groups of crystals. It melts at 155° and if cautiously heated solidifies without decomposition. It is nearly insoluble in *water*, but dissolves easily in *alcohol* and in *ether*. Boiling aqueous *ammonia* converts it into pyrotartronitranilic acid. *Fixed alkalis* determine the same transformation, part of the pyrotartranilic acid being however resolved by the further action of the alkali into pyrotartaric acid and β-nitraniline (see PHENYLAMINES, p. 445).

**PYROTARTRONITRANILIC ACID,** or *Nitrophenyl-pyrotartramic acid*,



$C^{11}H^{12}N^2O^5 = \left.\begin{matrix}H.C^6H^4(NO^2)\\(C^5H^6O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Arppe, *loc. cit.*)—When pyrotartronitranil is introduced into a slightly diluted and boiling solution of sodic carbonate, a yellow liquid is obtained, which, on cooling, deposits yellow crystals of β-nitraniline, whilst pyrotartronitranilate of sodium remains in solution; and on adding nitric acid to the filtered liquid, pyrotartranilic acid separates in yellowish flakes, which may be purified by recrystallisation.

Pyrotartronitranilic acid is very slightly soluble in water, but dissolves easily in alcohol and ether, and is deposited from a saturated solution in microscopic rhombic crystals of 120°. It melts at a little above 150°. It is a very feeble acid, being scarcely able to decompose carbonates.

The pyrotartronitranilates are unstable salts difficult to crystallise. The *silver-salt*, $C^{11}H^{11}AgN^2O^5$, is precipitated in white flocks.

**PYROTECHNY.** See Richardson and Watts's *Chemical Technology*, i. [4], 551 – 611; also Ure's *Dictionary of Arts*, &c., iii.

**PYROTEREBIC ACID.** $C^6H^{10}O^2 = \left.\begin{matrix}C^6H^9O\\H\end{matrix}\right\}O$. *Pyroterebilic acid. Brenzterebinsaure.*—This acid, belonging to the acrylic series, $C^nH^{2n-2}O^2$, and metameric with ethyl-crotonic acid (p. 273), was discovered by Rabourdin (J. Pharm. [3] vi. 196), and has been further examined by Chautard (*ibid.* xxviii. 192). It is produced by the dry distillation of terebic acid and purified by repeated rectification:

$$C^7H^{10}O^4 = CO^2 + C^6H^{10}O^2.$$

It is a liquid boiling at 210°, and smelling of butyric acid. It dissolves in 25 pts. of water, and is easily soluble in alcohol and ether. When gradually dropped into melting hydrate of potassium, it is resolved, with evolution of hydrogen, into acetic and butyric acids:

$$C^6H^{10}O^2 + 2H^2O = C^2H^4O^2 + C^4H^8O^2 + H^2.$$

*Pyroterebate of silver*, $C^6H^9AgO^2$, crystallises with difficulty, and blackens on exposure to light, especially when moist.

**PYRO-URIC ACID.** Syn. with CYANURIC ACID.

**PYROXAM.** Syn. with XYLOIDIN.

**PYROXANTHIN.** *Eblanin.* A yellow crystalline substance produced by the action of potash on one of the substances contained in heavy oil of wood-tar (Völckel). It is contained in crude wood-spirit, as first observed by Scanlan, and may be separated therefrom, according to Gregory (Ann. Ch. Pharm. xxi, 143), by distilling the liquid, collecting about 15 per cent., saturating the distillate with slaked lime, and redistilling. The residue, containing the excess of lime employed, acetate of calcium, a brownish resin, and pyroxanthin, is treated with dilute hydrochloric acid, and the insoluble portion is digested in boiling alcohol, which dissolves the resinous matter first; the pyroxanthin is found in the last alcoholic decoctions.

Pyroxanthin crystallises in long yellow needles, inodorous, insoluble in water, soluble with aid of heat in alcohol, ether, and acetic acid, nearly insoluble in ammonia and in boiling potash. It melts at 144°. When heated in a tube closed at one end, it does not volatilise without decomposition; but if heated in a current of air, it sublimes at 134°. Gregory found in it 74·8 per cent. carbon and 5·5 hydrogen, numbers agreeing nearly with the formula $C^5H^4O^2$, which requires 75 carbon, 5 hydrogen, and 20 oxyygen.

Pyroxanthin dissolves with deep red colour in strong sulphuric and in fuming hydrochloric acid; water precipitates it from the solution in a partly altered state. Strong nitric acid attacks it violently, converting it into oxalic acid and a nitro-compound. Chlorine, with aid of heat, converts it into a brown resinous substance, with disengagement of hydrochloric acid.

**PYROXANTHOGEN.** The constituent of wood-tar, from which pyroxanthin is supposed to be formed.

**PYROXENE.** A name sometimes used as synonymous with augite to denote the mineral species (i. 275), but more commonly restricted to certain varieties having a green or greyish-green colour. (Dana, ii. 158.)

**PYROXENITE.** A rock consisting of felspar and lamellar pyroxene.

**PYROXYLIN.** *Gun-cotton; Coton fulminant; Coton-poudre; Poudre-coton; Fulmi-coton. Schiessbaumwolle; explodirende Baumwolle.*—These names are applied to certain explosive substances produced by the action of fuming nitric acid, or of a mixture of nitric and sulphuric acids, on cotton wool. Schönbein, in 1845, announced the discovery of an explosive cotton-wool applicable as a substitute for gunpowder, but his mode of preparation was at first kept secret; and soon afterwards the method of producing the explosive compound by treating cotton-wool with strong nitric acid was discovered independently by Böttger and Otto, and published by the latter (Augsburg, Allg. Zeitung, Oct. 5, 1846; J. pr. Chem. xi. 193). Knop (Compt. rend. xxiii. 808) soon afterwards introduced the more advantageous method of treating the cotton-wool with a mixture of strong nitric and sulphuric acids. The chemical composition and properties of pyroxylin have been made the subject of numerous researches by **Böttger**, **Pelouze**, **Payen**, **Peligot**, **van Kerckhoff**, **Sobrero**, **Béchamp**, and others on the continent, and in this country by **Porrett**, **Ransom**, **Crum**, **Gladstone**, and **Hadow**. (For a complete list of memoirs relating to it, down to 1862, see Gmelin's *Handbook*, xv. 168.) From its first discovery, also, numerous experiments were made on its applicability to military and mining operations as a substitute for gunpowder, over which it possesses the great advantage of burning without smoke, and leaving no residue to foul the gun; and its preparation was soon commenced on a large scale; but the occurrence of several severe and unexplained accidents during the manufacture, attended with great loss of life, caused it to be regarded as too dangerous and unmanageable for military purposes, and accordingly its manufacture was for a while nearly given up. Within the last few years, however, the attempts to make use of gun-cotton as a substitute for gunpowder have been renewed, and brought to a successful issue chiefly by the investigations of **General von Lenk**, an Austrian officer of artillery, who has discovered the cause of previous failures, gradually perfected the process of manufacture, and instituted, under the auspices of the Austrian government, an elaborate series of experiments on the best methods of applying it to gunnery.

Cotton treated with a mixture of nitric and sulphuric acids, yields a number of products which may be regarded as cellulose, $C^6H^{10}O^5$, in which the hydrogen is more or less replaced by nitric peroxide, $NO^2$, the degree of nitration varying according to the mode of preparation. The different compounds have different degrees of stability and are variously affected by solvents. According to **Hadow** (Chem. Soc. Qu. J. vii. 201), the three principal products are:

*α*. $C^{18}H^{21}(NO^2)^9O^{15}$ or $C^6H^7(NO^2)^3O^5$, insoluble in a mixture of ether and alcohol; but soluble in ethylic acetate. It is produced by repeated immersion of cotton-wool in a mixture of 2 at. nitric acid, $HNO^3$, 2 at. oil of vitriol, $H^2SO^4$, and 3 at. water.

*β*. $C^{18}H^{22}(NO^2)^8O^{15}$, soluble in ether-alcohol, insoluble in glacial acetic acid. Produced when the acid mixture contains ½ at. more water than in *α*.

*γ*. $C^{18}H^{23}(NO^2)^7O^{15}$ (Gladstone's *cotton-xyloïdin*), soluble in ether and in glacial acetic acid. Produced when the acid mixture contains 1 at. more water than in *α*.

The term "pyroxylin" is sometimes applied especially to the more highly nitrated compounds; but it is much better to use this term as a generic name for all the substitution-compounds formed by the action of nitric acid on cellulose, and to designate as "gun-cotton" the most highly nitrated compound, **trinitrocellulose**, $C^6H^7(NO^2)^3O^5$, which is the only one adapted for use in gunnery.

The lower compounds, which are soluble in alcohol and ether, are used for the preparation of collodion (i. 1083).

### *Gun-cotton.* $C^6H^7(NO^2)^3O^5$.

When cotton-wool is immersed in a mixture of strong nitric and sulphuric acids, substitution takes place immediately, and the product has only to be freed from adhering acid by washing with water and then dried. But in order to insure the uniform production of the most highly nitrated compound, Lenk adopts several precautions, the most important of which are:

1. The cleansing and perfect desiccation of the cotton previously to its immersion in the mixed acids.
2. The employment of the strongest acids procurable in commerce.
3. The steeping of the cotton in a fresh strong mixture of acids after the first immersion and partial conversion into gun-cotton.
4. The continuance of the steeping for forty-eight hours.
5. The thorough purification of the gun-cotton thus produced from every trace of free acid, by washing the product in a stream of water for several weeks; subsequently a weak solution of potash may be used, but this is not essential.

The prolonged application of these processes is absolutely necessary to ensure the thorough nitration of the cotton and the subsequent purification of the product; for each cotton-fibre is a long narrow tube, often twisted and even doubled up, and the acid has first to penetrate to the inmost depths of these tubes and afterwards to be soaked out of them: hence the necessity of time.

Sometimes, to render the gun-cotton less explosive, and to remove the last lingering traces of free acid, it is impregnated with a solution of silicate of sodium (soluble glass), which is forced into it by means of a centrifugal machine, having a central tube for supplying the solution. It is then dried by exposure to the air, whereby carbonate of sodium is formed, and silica separated, and the carbonate of sodium is afterwards washed out with water, while the silica remains attached to the fibres.

Sometimes, again, to render the fibres soft and diminish the danger of explosion from violent friction, the gun-cotton, after being treated with soluble glass, is immersed in a soap-ley, the excess of which is then squeezed out, and the gun-cotton finally dried.

For details of the Austrian process, and of experiments on the preparation of gun-cotton at the Royal Gunpowder Works at Waltham Abbey, see the article "Gun-cotton" by Dr. **Gladstone** in Richardson and Watts's *Chemical Technology*, i. [4] 487—500. Gun-cotton is now prepared on a large scale by a process essentially the same as that of Lenk, at the manufactory of Messrs. Prentice at Stowmarket.

Gun-cotton prepared by the process just described retains the external properties of cotton-wool, but is somewhat harsher to the touch, unless it has been soaped. It has neither taste nor smell, and is neutral to moistened litmus-paper. By friction it becomes more strongly electric than cat's skin; it crackles, yields sparks, and is phosphorescent in the dark (**Gaiffe**, Compt. rend. xxiv. 88). Its fibres seen under the microscope by polarised light, exhibit very little brightness, and scarcely any play of colours, whereas the fibres of ordinary cotton-wool appear bright and show a fine play of colours even in the dimmest light. (**Kindt**, Pogg. Ann. lxx. 168.)

The following analyses of Lenk's gun-cotton, the first made in the laboratory of the Imperial Engineers' Committee, the second in the University laboratory at Vienna, show that it consists of trinitrocellulose, $C^6H^7(NO^2)^3O^5$.

| | *Calculation.* | | *Analyses.* | | | |
|---|---|---|---|---|---|---|
| $C^6$ . . . | 72 | 24·3 | 25·1 | 24·4 | 24·4 | 23·9 |
| $H^7$ . . . | 7 | 2·3 | 3·0 | 2·7 | 2·6 | 2·4 |
| $N^3$ . . . | 42 | 14·1 | | | | |
| $O^{11}$ . . . | 176 | 59·3 | | | | |
| | 297 | 100·0 | | | | |

Gun-cotton is insoluble in water, and perfectly unaffected by long soaking in that liquid. It usually absorbs about 2 per cent. of hygroscopic moisture, any excess that it may absorb under peculiar atmospheric conditions being speedily given off when the air returns to its ordinary state of dryness. It is insoluble also in alcohol, ether, and glacial acetic acid.

Gun-cotton is not affected by dilute acids or alkalis; but *nitric acid* of specific gravity 1·45 attacks it, producing a lower substitution-product which weighs only $\frac{4}{5}$ths of the original trinitrocellulose. Strong *sulphuric acid* dissolves it with some difficulty, and the solution does not turn black even when heated to a high temperature, though it then gives off carbonic anhydride and nitric oxide.

Strong *potash-ley* dissolves gun-cotton rapidly, especially if heated to about 70°, with formation of ammonia, nitrous acid, oxalic acid, and other acids. The alkaline solution reduces an ammoniacal solution of silver, and has in fact been used for silvering mirrors.

A solution of *potassic sulphydrate*, especially if mixed with alcohol, reproduces the original cotton, with formation of potassic nitrate and a little ammonia.—*Ferrous sulphate* exerts a similar reducing action, likewise reproducing the original cotton (**Béchamp**). Gun-cotton placed in contact with *sulphuric acid* and metallic *mercury*, gives off all its nitrogen in the form of nitric oxide. On account of these last three reactions, gun-cotton is regarded by Béchamp, Pelouze, Crum, and other chemists, as analogous in constitution to a nitric ether, rather than to such compounds as nitrobenzene, nitrobenzoic acid, &c., inasmuch as the latter, when treated with reducing agents, are converted into other compounds containing nitrogen, whereas gun-cotton, like the nitric ethers and nitrates in general, is deprived by these reagents of the whole of its nitrogen, and in some cases reconverted into the original cotton-wool.

Gun-cotton is a remarkably stable substance, but nevertheless appears under certain circumstances to undergo a slow spontaneous decomposition. It has been stored in Austria for twelve years in wooden boxes without exhibiting any sign of alteration; and some that was taken to Italy in 1859, and thrown aside where it was exposed for a long time to a hot sun in black boxes, was afterwards found unaltered. Some varieties of gun-cotton, however, when enclosed together with litmus-paper in a tube, exhibit an acid reaction even at ordinary temperatures. The more completely the free acid has been removed, the less does the gun-cotton appear to be liable to spontaneous decomposition either slow or sudden; and in this, according to some authorities, consists the advantage of washing the gun-cotton with an alkaline solution or impregnating it with soluble glass. (See Gmelin's *Handbook*, xv. 175; *Chemical Technology*, i. [4] 500; also **Melsens**, Bull. Soc. Chim. 1865, i. 35.)

Gun-cotton prepared by Lenk's process is not liable to explosion by percussion; it may detonate between iron and iron if a heavy blow be struck, but only that part explodes which was hit, without communicating ignition to the surrounding particles.

If a heavy blow be struck on gun-cotton with an iron hammer upon bronze or any other comparatively soft metal, or upon stone, no detonation takes place. Otto found, on the other hand, that pyroxylin prepared with nitric acid alone, explodes like fulminating mercury when struck with a hammer.

The temperature at which gun-cotton explodes has been very accurately determined by Baron Von Ebner, who fixes the lowest temperature at 136° C. (277° Fahrenheit); but the heat required is usually stated to be greater than this. According to Melsens gun-cotton which has been washed with soda and retains a small quantity of the alkali, does not explode till heated to 180°, and similar observations have been made by Payen, Pelouze, Piobert, Van Kerckhoff and others.

On explosion, gun-cotton is almost entirely resolved into gases, leaving only about 1 per cent. of natural mineral constituents, the small amount of silica, if it has been silicated, and possibly a trace of carbon.

Lieutenant Van Karolyi (Phil. Mag. [4] xxvi. 272) has fully investigated the products of the combustion of gun-cotton and gunpowder, under circumstances analogous to those which occur in practice. In his first experiments, he exploded the gun-cotton in a Torricellian vacuum, made in a eudiometer about a metre in length, across which was drawn a very thin platinum wire, that could be ignited by a galvanic battery. The gases were analysed in the usual manner, with the following results:

| | By volume. | By weight. |
|---|---|---|
| Carbonic oxide | 28·55 | 28·92 |
| Carbonic anhydride | 19·11 | 30·43 |
| Marsh gas | 11·17 | 6·47 |
| Nitric oxide | 8·83 | 9·59 |
| Nitrogen | 8·56 | 8·71 |
| Carbon | 1·85 | 1·60 |
| Aqueous vapour | 21·93 | 14·28 |
| | 100·00 | 100·00 |

It was found that, on exploding a somewhat larger quantity of gun-cotton under the same circumstances, when therefore the combustion takes place under comparatively greater pressure, the proportional quantities of the products change, and the quantity of nitric oxide diminishes. Hence the deoxidation of the nitrogen-compounds during the combustion takes place more completely, the greater the work which the gun-cotton has to perform while exploding. This circumstance suggested to Karolyi the idea of exposing the gun-cotton during its combustion to a resistance so regulated that it just gives way at the moment when the gun-cotton is completely burnt. He therefore placed a vessel filled with gun-cotton, which offered the necessary resistance, in a sixty-pound mortar, which was then exhausted, and the gun-cotton was exploded by a thin platinum-wire heated to redness by the electric current. An analysis of the gases produced under these circumstances gave the following numbers:

| | By volume. | By weight. |
|---|---|---|
| Carbonic oxide | 28·95 | 29·97 |
| Carbonic anhydride | 20·82 | 33·86 |
| Marsh gas | 7·24 | 4·28 |
| Hydrogen | 3·16 | 0·24 |
| Nitrogen | 12·67 | 13·16 |
| Carbon | 1·82 | 1·62 |
| Aqueous vapour | 25·34 | 16·87 |
| | 100·00 | 100·00 |

It will be observed that in this latter case, which is analogous to what takes place in practice, no nitric oxide is formed, but a certain amount of hydrogen, and a larger proportion of nitrogen and aqueous vapour. When exploded in this manner, 10 grammes of gun-cotton was found to yield 57·40 cubic centimetres of gas, at 0° C. and 1 metre pressure. These gases are combustible, on account of the large quantity of carbonic oxide they contain.

For the results obtained by Karolyi from gunpowder burnt in a similar manner, see ii. 958, 959.

Abel (Proc. Roy. Soc. xiii. 204) has made a series of ingenious experiments on the combustion of gun-cotton. He finds that when quantities of gun-cotton, varying from one to two grains, in the form of a loose twist laid double, are ignited by means of a platinum wire in highly rarefied atmospheres, they burn very slowly, presenting by daylight an appearance as if they smouldered. The pressure in the case described must not exceed 8 inches of mercury; but the rarefaction necessary for the result varies with the quantity of gun-cotton, its mechanical condition, its position with reference to the source of heat, the quantity of heat applied, and the duration of its application.

Gun-cotton, when ignited in small quantities in rarefied atmospheres, may exhibit, during its combustion, three distinct luminous phenomena. In the most highly rarefied atmospheres, the only indication of combustion is a beautiful green glow, or phosphorescence, which surrounds the extremity of the gun-cotton as it is slowly transformed into gases or vapours. When the pressure of the atmosphere is increased to one inch (with the proportion of gun cotton indicated), a faint yellow flame appears at a short distance from the point of decomposition; and as the pressure is increased, this pale yellow flame increases in size, and eventually appears quite to obliterate the green light. Lastly, when the pressure of the atmosphere and consequent proportion of the oxygen in the confined space is considerable, the cotton burns with the ordinary bright yellow flame. There can be no doubt that this final result is due to the almost instantaneous secondary combustion, in the air supplied, of the inflammable gases evolved by the explosion of the gun-cotton. The pale yellow flame will take place in rarefied nitrogen.

In a series of experiments made under gradually diminished pressures, oxygen being used instead of air, it was found that the gun-cotton exploded instantaneously, with a bright flash, until the pressure was reduced to 1·2 inch; from this pressure to that of 0·8 inch it still burned with a flash, but not instantaneously; and at pressures below 0·8 inch it no longer burned with a bright flash, but exhibited the comparatively slow combustion, accompanied by the pale yellow flame. In atmospheres of carbonic anhydride, carbonic oxide, hydrogen, and coal-gas, this pale yellow flame is seen as in nitrogen; but the two latter gases have a great tendency to extinguish the combustion, doubtless on account of their high cooling powers by convection.

The slow kind of combustion of gun-cotton, in the form of twist, may be obtained also in a powerful current of atmospheric air, if the thread of cotton be placed in a somewhat narrow glass tube. Indeed, it was found that if, even for the briefest space of time, the gases resulting from the first action of heat on gun-cotton upon its ignition in open air are impeded from completely enveloping the burning extremity of the gun-cotton twist, their ignition is prevented, and the gun-cotton continues to burn in the slow and imperfect manner, undergoing a transformation similar in character to destructive distillation. By proper arrangements, these gases may be burnt at the mouth of a tube while the gun-cotton is burning in the interior. There is little doubt that these products of decomposition vary as greatly as the phenomena themselves: thus, in the instances of the most imperfect metamorphosis of gun-cotton, the products included a considerable proportion of a white vapour, slowly dissolved by water, as also small quantities of nitrous acid, and a very large proportion of nitric oxide; cyanogen, too, is always found. This contrasts greatly with the simpler products of decomposition found by Karolyi when the gun-cotton was exploded under the pressure of a confined space.

Abel considers that the remarkable facility with which the combustion of gun-cotton in air or other gases may be modified, might be taken advantage of to produce a variety of mechanical effects; and he states, that by enclosing in suitable cases solid cords made up of two or more strands of gun-cotton, more or less compactly twisted, he has succeeded in producing fuses and slow-matches, the time of burning of which may be accurately regulated.

*Practical Application to Gunnery.*—Gun-cotton is used for artillery in the form of thread or spun-yarn. In this simple form it will conduct combustion slowly in the open air at the rate of not more than 1 foot per second. This thread is woven into a texture or circular web. These webs are made of various diameters; and from them common rifle cartridges are made, merely by cutting them into the proper lengths, and enclosing them in stiff cylinders of pasteboard, which form the cartridge. In this shape its combustion in the open air takes place at a speed of 10 feet per second.

The gun-cotton yarn is used directly to form cartridges for large guns, by being wound round a bobbin, so as to form a spindle like that used in spinning mills. The bobbin is a hollow tube of paper or wood. The object of the wooden rod is to secure in all cases the necessary length of chamber required for the most effective explosion. (For figures see *Chemical Technology*, i. [4] 506.)

Practically, gun-cotton is most effective in guns when used as $\frac{1}{4}$ to $\frac{1}{3}$ weight of powder, and occupying a space of $\frac{11}{10}$ths of the length of the powder-cartridge, and of such density that 11 lbs. occupy a cubic foot.

Lenk's gun-cotton, when used as a substitute for powder, is found to possess the following advantages: 1. Greater safety during the manufacture.—2. The possibility of keeping it under water at any time, or of immersing it on any sudden emergency, without damaging it.—3. Its being uninjured by damp.—4. Easier and safer conveyance, inasmuch as one ton of gun-cotton does the work of at least three tons of gunpowder; and there is no fear of the dangerous "getting to dust," and spilling.—5. The force of its explosion can be regulated so as to produce various results desired. According to its mechanical condition, it may be made to have any speed of explosion, from 1 foot per second to 1 foot in $\frac{1}{1000}$ of a second, or to instantaneity. The instantaneous explosion of a large quantity of gun-cotton is made use of when it is required to produce destructive effects on the surrounding material; the slow combustion, when it is required to produce manageable power, as in the case of gunnery.—6. It leaves no residue in the gun on explosion.—7. It produces no smoke.—8. The gases produced on explosion are less injurious to the gun, and to the men serving it.—9. It does not heat the gun so much.—10. It produces smaller recoil, only two-thirds of that from gunpowder, the projectile effect being equal. This depends probably to a certain extent on the solid residue of exploded gunpowder having to be projected in addition to the shot, and, as is generally thought, at much higher speed. The remainder, General Von Lenk attributes to a different law of combustion. On account of the smallness of recoil, a lighter and shorter gun may be employed.

On the other hand, gun-cotton has some disadvantages as compared with gunpowder. 1. It is suspected of being liable to spontaneous decomposition under certain unknown circumstances.—2. It ignites at a lower temperature.—3. For use in guns, it requires greater care and precision in the manufacture of the cartridge, lest its great power should be exerted in rending the piece, rather than propelling the ball.

*Application to other Military Purposes.*—However suitable gun-cotton may seem to be as a source of projectile power, it is still better adapted to other purposes for which an explosive is required. Indeed, its capability of instantaneous explosion enables it to perform easily some descriptions of work, which gunpowder could scarcely, if at all, accomplish.

The condition necessary to produce instantaneous and complete explosion, is the absolute perfection of closeness of the chamber containing the gun-cotton. The reason of this is, that the first ignited gases must penetrate the whole mass of the cotton; and this they do, and create complete ignition throughout, only under pressure.

For *fuses*, gun-cotton is woven into a web, steeped in saltpetre, and covered with an Indian-rubber jacket. The combustion of this takes place at about 30 feet per second, and produces a sharp noise, heating but not tearing the jacket. Such a fuse will fire although a considerable weight be placed upon it, and it may be doubled up without fear of the fire communicating from fold to fold. If ordinary gun-cotton thread be fired, ignition takes place at the rate of only about one foot per second.

*Shells* with holes are easily filled with gun-cotton web, and projectiles that open may be charged with compressed gun-cotton. In this way a much larger amount of force may be stored up in the shell than with gunpowder; consequently it bursts into double the number of pieces; and it is said that the stronger the shell, the smaller are the fragments into which it is broken. "It is a well-known fact, that a bag of gunpowder nailed on the gates of a city will blow them open. In this case gun-cotton would fail; a bag of gun-cotton exploded in the same way is powerless. To blow up the gates of a city, a very few pounds of gun-cotton carried in the hand of a single man will be sufficient: only he must know its nature:—in a bag, it is harmless; exploded in a box it will shatter the gates to atoms." A small box containing gun-cotton, merely flung down close to palisades, and exploded by a galvanic battery or a fuse, will open a passage for troops.

The same force has been applied to the destruction of bridges. "A strong bridge of oak, 12 inches scantling, 24 feet span, was shattered to atoms by a small box of 25 lbs. laid on its centre: the bridge was not broken, it was shivered."

For military mining the gun-cotton charge is placed in little barrels with strong hoops.

The effect of gun-cotton, when exploded under water, is very remarkable. The action is so instantaneous that the water has no time to yield, and thus it is unnecessary to place the charge in contact with the body to be destroyed, as is said to be the case when gunpowder is used. "Two tiers of piles, 10 inches thick, in water 13 feet deep, with stones between them, were blown up by a barrel of 100 lbs. of gun-cotton placed 3 feet from the face and 8 feet under water. It made a clean sweep through a radius of 15 feet, and raised the water 200 feet. The iron anchor used to keep the box in position was found broken across. At the close of the Italian campaign, some experiments on ships were made at Venice, in the presence of the Emperor of Austria. In one of these, a barrel of 400 lbs weight was placed near a sloop in 10 feet of water, the nearest part of the hull of the vessel being about 18 feet distant; yet the sloop was broken to pieces, and these were hurled into the air to the height of 400 feet. This kind of explosion is attended with terrific noise. It was observed that the fishes, for perhaps half a mile round, were stunned, and floated on the surface. They recovered after awhile, but not till many had been picked up by hand."

*Application to Blasting.*—Gun-cotton thread is spun into ropes in the usual way, up to two inches diameter, hollow in the centre. This is the form used for blasting and mining purposes; it combines great density with speedy explosion, and in this form the gun-cotton is conveniently coiled in casks and stowed in boxes. The fact that the action of gun-cotton is violent and rapid in exact proportion to the resistance it encounters, tells us the secret of its far higher efficacy in mining than gunpowder. The stronger the rock, the less gun-cotton, comparatively with gunpowder, is necessary for the effect; so much so, that while gun-cotton is stronger than powder as 3 to 1 in artillery, it is stronger in the proportion of 6·274 to 1 in a strong and solid rock, weight for weight. Its power of splitting up the material can be regulated at will. As it is not liable to be spilt about by the miners like powder, there is less danger of accidental explosion. The absence of smoke in its explosion, also, conduces to the comfort of the workmen.

### *Pyroxylin for the preparation of Collodion.*

It has already been stated that the highest nitro-substitution product of cotton, namely trinitrocellulose, $C^6H^7(NO^2)^3O^5$, does not dissolve in a mixture of ether and alcohol, but that the lower compounds are capable of doing so. It is these compounds, therefore, that are alone available for making that solution of gun-cotton, which is known by the name of collodion. They are produced when weaker acids are employed, or when the precautions mentioned above in the preparation of Lenk's gun-cotton are not observed (p. 779).

These lower nitro-substitution products of cellulose do not resemble the original cotton in appearance so closely as the highest compound does; for they show more signs of the action of the acid on the fibre. Indeed, there is at least one compound which is soluble in nitric acid, whether fuming or of as low a specific gravity as 1·25, and may be precipitated as a granular powder on the addition of water.

They explode at a lower temperature than trinitrocellulose, but this temperature depends both upon the nature of the compound and the manner in which the heat is applied. A long-continued heat will explode a mass of such pyroxylin which at first was not set on fire; and there can be little doubt that under such circumstances it may be exploded at a temperature very little exceeding that of boiling water; indeed, much lower temperatures have been mentioned by some observers.

These lower compounds, when exploded, leave a certain amount of carbonaceous residue.

All these substitution-products dissolve in strong sulphuric acid, but a solution of cotton-xyloïdin, $C^{18}H^{23}(NO^2)^7O^{15}$, in that acid, is charred at as low a temperature as 180° Fahrenheit.

These lower compounds are liable to spontaneous decomposition, which takes place very slowly at first, but when it has reached a certain point, perhaps after the lapse of several years, the action becomes much more rapid. The spontaneous explosions which have sometimes taken place with ill-prepared gun-cotton, may with great probability be attributed to the presence of these lower compounds. It does not appear to be proved that any pyroxylin ever *explodes* without extraneous heat. Light certainly favours this decomposition, but is not indispensable, for it is on record, that pyroxylin stowed away in casks has evolved a choking smell after some months. The usual progress of decomposition is of this character:—the pyroxylin begins to emit a peculiar odour, rather agreeable than otherwise; the gas increases, perhaps driving out the stopper, if the pyroxylin be contained in a stoppered bottle; the cotton becomes damp, and shrinks together; and, as decomposition goes on, the fibre disappears, and there remains a gummy mass, probably interspersed with crystals. The gases include nitric oxide, and apparently, in some cases, prussic acid. The crystals consist of oxalic acid, and the residue is a mixture of products consisting of water, nitric acid, and several organic acids not always soluble in water.

The pyroxylin used for the preparation of collodion is not a definite compound, but a mixture of two or more varieties of nitrocellulose. It may be prepared by treating cotton-wool either with oil of vitriol and nitrate of potassium, or with a mixture of strong nitric and sulphuric acids. In the former case, 60 grains of cotton-wool pulled out into separate balls of about the size of a walnut, is immersed in a mixture of 6 fluid ounces of oil of vitriol, 3½ oz. (avoird.) of dried saltpetre, and 1 fluid ounce of water. The cotton must be well stirred about in the liquid, kept at the temperature of 140° Fah. for about two minutes, then suddenly thrown into cold water, and briskly moved about till thoroughly washed. When nitrosulphuric acid is used, larger quantities may be operated upon at once: viz. 400 grains of cotton-wool, 6 fluid ounces of nitric acid of specific gravity 1·45, 18 fluid ounces of oil of vitriol of specific gravity 1·84, and 4½ ounces of water. In this, as in the former case, very rapid washing is necessary, otherwise spontaneous decomposition will take place, attended with evolution of red

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fumes. For details of manipulation see Hardwich's *Manual of Photographic Chemistry;* also *Technology*, i. [4] 513. The properties and uses of collodion have been already described (i. 1084).

**PYRRHITE** (from πυῤῥος, yellow) is the name given by G. Rose to a mineral occurring at Mursinsk in the Ural, in small orange-yellow octahedrons; also by Teschemacher to a perfectly similar mineral from the Azores, which, according to Hayes, consists chiefly of niobate of zirconium. (Dana, ii. 346.)

**PYRRHOL.** Syn. with PYRROL.

**PYRRHOPINE.** This name was given by Polex (Berz. Jahresb. xix. 433) to an alkaloïd extracted by alcohol from the root of *Chelidonium majus*, and distinguished by forming red sparingly soluble salts with acids. It is doubtless identical with chelerythrine (i. 847).

**PYRRHORETIN.** A brown humus-like substance found by Forchhammer in the fossil pine-wood of Denmark, and regarded by him as a humate of boloretin (i. 619). It is soluble in alcohol, insoluble in ether, and when its alcoholic solution is mixed with a quantity of ether, not sufficient to produce a precipitate, and ammonia then added, humate (ulmate) of ammonium is said to be precipitated, while boloretin remains in solution. The substance appears however to be merely a mixture (Handw. d. Chem. vi. 739).

**PYRRHOSIDERITE.** Syn. with GÖTHITE.

**PYRRHOTIN.** Magnetic pyrites. (See IRON, SULPHIDES OF, iii. 401.)

**PYRROL.** $C^4H^5N$. (Runge, Pogg. Ann. xxxi. 67.—Anderson, Ed. Phil. Trans. xx. [2] 247; xxi. [4] 571.—Schwanert, Ann. Ch. Pharm. cxv. 279.)

*History.*—Runge was the first to observe that the products of the destructive distillation of coal contained a substance which caused fir-wood moistened with hydrochloric acid to assume a red colour. It is not necessary to moisten the wood with the liquid to be tried, it is sufficient to hold it over the liquid containing the pyrrol. Runge considered pyrrol to be a gas, but he never prepared it in a pure state.

*Formation.*—1. Pyrrol appears to be produced in almost every instance where animal or vegetable matters containing nitrogen are subjected to destructive distillation (Gr. Williams).—2. It is also produced in considerable quantity by the destructive distillation of mucate of ammonium, occurring as a product of decomposition of the dipyromucamide (carbopyrrolamide) formed in the first stage of the decomposition (p. 765).—3. By heating carbopyrrolic acid, $C^5H^5NO^2$, which is resolved thereby into pyrrol and carbonic anhydride (p. 764).

*Preparation.* 1. From bone-oil.—The oil is shaken up with dilute hydrochloric or sulphuric acids, and the acid solution is distilled. A portion of the pyrrol is thereby destroyed, but the greater portion distils over in an impure state. By repeated fractional distillation it may be obtained with a boiling point between 132° and 143°. It is then to be several times shaken up with dilute acids, to remove picoline and other basic impurities. After drying by means of sticks of potassium, it is again fractionally distilled until it boils almost entirely between 134° and 138°. In this state it gives tolerably correct numbers on analysis, but it is still contaminated with some impurities which give it an offensive odour. It must therefore be cohobated over solid hydrate of potassium until little or no liquid is seen to rise in the cohobating tube, even although the bottom of the flask is heated almost to redness. The cohobating tube is then replaced by a bent tube, and all volatile matters are distilled away; the residue in the flask is poured out on to a metal plate and allowed to cool; and the compound of pyrrol with potash is decomposed with water, when the pure pyrrol will rise to the surface in the form of a fragrant colourless oil, which may be dried by digestion with sticks of potash. On rectification the pure pyrrol will come over steadily at 133°. (Anderson.)

2. From mucate of ammonium.—When this salt in the state of dry powder is distilled, crystals of carbonate of ammonium are obtained, together with an aqueous solution of carbopyrrolamide and a brown oil chiefly consisting of pyrrol floating thereon; and by washing this oil with water, dehydrating it with solid potash and rectifying it after standing over chloride of calcium, the pyrrol is obtained pure. This is a much easier mode of preparation than the former. Carbopyrrolic acid (p. 761) does not yield pure pyrrol quite so easily, because a portion of it sublimes undecomposed. (Schwanert.)

*Properties.*—Colourless transparent liquid of delightfully fragrant odour resembling chloroform, but softer and less pungent. Boils at 133°. Tastes hot and pungent. Sparingly soluble in *water*, but is readily soluble in *alcohol*, *ether*, and *oils*. Insoluble

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in alkaline solutions; dissolves, but not readily, in *acids*. Specific gravity of liquid 1·077, of vapour 2·40.

*Decompositions.*—1. Colourless pyrrol soon becomes brown by keeping; it may, however, always be re-obtained colourless by distillation. 2. A piece of fir-wood moistened with hydrochloric acid rapidly acquires an intense carmine colour when exposed to even the minutest traces of pyrrol vapour. One drop of pyrrol will confer upon the air of a large jar the power of giving this reaction. 3. When agitated with dilute *acids* in the cold, pyrrol dissolves unchanged, but, on heating the solution, a red flocculent substance called pyrrol-red (*infra.*), is formed in such quantity that the vessel may be inverted without the contents escaping.—4. Solution of *platinic chloride* added to a cold hydrochloric solution of pyrrol causes the solution to become instantly dark coloured, and in a few minutes an abundant black precipitate, containing platinum, but of indefinite composition, is deposited.—5. Solution of *ferric chloride* causes the hydrochloric solution of pyrrol to become first green and then black.—6. *Dichromate of potassium* also decomposes a similar solution with formation of an abundant black precipitate.—7. Pyrrol is rapidly oxidised by *nitric acid*, red fumes are given off, and, if the action is prolonged, oxalic acid is formed.

8. Alcoholic solution of pyrrol gives a white precipitate with mercuric chloride, and also with chloride of cadmium, but it does not precipitate the metallic oxides generally.

The *mercury-salt*, $C^4H^5N.2Hg''Cl^2$, is a white crystalline powder insoluble in water, sparingly soluble in cold alcohol: the solution is probably decomposed on boiling.—The *cadmium-salt*, $4C^4H^5N.3Cd''Cl^2$, is a white crystalline powder insoluble in water, but readily soluble in hydrochloric acid.

Pyrrol does not form any definite compounds with *acids*, although it is decidedly basic. At a red heat it unites with *hydrate of potassium*, but the compound is decomposed by mere solution in water. C. G. W.

**PYRROL-RED.** $C^{12}H^{14}N^2O$.—When pyrrol is warmed or boiled with excess of sulphuric or hydrochloric acid, this substance separates in amorphous orange-red or brown flocks, the colour of which is darker, in proportion as the action of the acid has been longer continued. It is also produced when carbopyrrolic acid or its barium-salt is heated to 60° or above with acids, the carbopyrrolic acid being thereby resolved into carbonic anhydride and pyrrol, a portion of which is then converted into pyrrol-red as above.

Pyrrol-red is insoluble in water and in ether, but somewhat soluble in hot alcohol; insoluble in acids and in alkalis. Anderson found it to contain 71·98 per cent. carbon, 6·88 hydrogen, 13·59 nitrogen and 7·55 oxygen, agreeing nearly with the above formula which requires 71·28 C, 6·93 H, 13·86 N, and 7·93 O. Schwanert found in pyrrol-red from carbopyrrolic acid, proportions of carbon and nitrogen smaller than these. According to Anderson's formula, the formation of pyrrol-red from pyrrol may be represented by the equation,

$$3C^4H^5N + H^2O = C^{12}H^{14}N^2O + NH^3.$$

**PYRUVIC ACID.** Syn. with PYRORACEMIC ACID (p. 769).

# ADDENDUM.

**NIOBIUM.** The recent investigations of Marignac (Compt. rend. lx. 234, 1355; Ann. Ch. Pharm. cxxxv. 49; cxxxvi. 29; Archives des Sciences physiques et naturelles, xxiii. 278), and of Deville and Troost (Compt. rend. lx. 1221; Ann. Ch. Pharm. cxxxvi. 249), have thrown an entirely new light on the constitution of the niobium-compounds. The principal results of these investigations are as follows:

1. There is but one oxide of niobium, namely that called *hyponiobic acid* by Rose, *niobous oxide* in this work (p. 53). The formula of this oxide, designated by Marignac as niobic acid, is $Nb^2O^5$. Rose's niobic (originally pelopic) acid, $NbO^2$, was a mixture of this compound with tantalic acid, having been prepared from columbites containing tantalum as well as niobium.

Marignac, by treating the so-called hyponiobic acid obtained from Greenland columbite (specific gravity = 5·36) with hydrofluoric acid, and neutralising the resulting fluoride with potash, obtained a fluoxyniobate of potassium, $2KF.NbOF^3$, without any trace of tantalum-salt; but on repeating the experiment with columbite from Haddam in Connecticut (specific gravity = 5·85), and from Bodenmais in Bavaria (specific gravity = 6·06), he obtained, in addition to the fluoxyniobate, a quantity of fluotantalate of potassium, greater as the specific gravity of the columbite was higher. Now as the Bavarian columbite used by Rose in his experiments had a high specific gravity (= 6·39), it probably contained a very considerable proportion of tantalic acid, so that all the compounds prepared from it would contain tantalum as well as niobium. (See TANTALUM.)

Pure niobic oxide, $Nb^2O^5$, has a specific gravity of 4·4—4·5. The higher density found by Rose (5·2 to 6·5) was due to the presence of tantalic oxide. All attempts to convert it into a higher or lower oxide have hitherto yielded only negative results. Its atomic weight, determined by Marignac from the analysis of the fluoxyniobates (*infra*) is 268, and therefore that of niobium 94.

2. The white chloride of niobium (Rose's *hyponiobic chloride*, also called *niobous chloride*, p. 50) is an oxychloride, $NbOCl^3$, containing, according to the analyses of Deville and Troost, 4 32 per cent. niobium, 48·9 chlorine and 7·3 oxygen, the formula requiring 43·3 niobium, 49·4 chlorine and 7·3 oxygen. The vapour-density of this oxychloride, as determined by experiment, is 7·9; calculation from the formula $NbOCl^3$ gives $\frac{94 + 16 + 3\,.\,35{\cdot}5}{2} \times 0{\cdot}0693 = 7{\cdot}5$.

This compound is instantly converted by water into niobic oxide, $Nb^2O^5$.

The yellow chloride (Rose's *pelopic*, afterwards *niobic, chloride*) obtained as described at page 50 from pure niobic oxide, is a pentachloride, $NbCl^5$. A specimen prepared by Deville and Troost, was found by Marignac to yield, when decomposed by aqueous ammonia, 65·28 pts. chlorine to 49·39 niobic oxide, calculation requiring 65·38 chlorine to 49·35 niobic oxide. Its vapour-density, according to the latest determination of Deville and Troost, is 9·6; calculation gives $\frac{94 + 5\,.\,35{\cdot}5}{2} \times 0{\cdot}0693 = 9{\cdot}4$.

This chloride, when treated with water, yields niobic oxide, $Nb^2O^5$, identical with that obtained from the white oxychloride.

3. *Niobates.*—These salts crystallise readily and in well-defined forms. Marignac has obtained several *niobates of potassium*. By fusing the oxide with 2 or 3 pts. of potassium-carbonate and evaporating the solution of the fused mass in a vacuum, large monoclinic prisms are obtained, containing $4K^2O.3Nb^2O^5.16H^2O$, and giving off 12 at. water at 100°. This salt, when heated to redness, becomes partially insoluble in water, and the solution yields by slow evaporation, pyramidal monoclinic crystals containing

$8K^2O.7Nb^2O^5.32H^2O$. A solution of either of the preceding salts mixed with caustic potash, and slowly evaporated, yields rhomboïdal prisms containing $3K^2O.2Nb^2O^5.13H^2O$. If the potash used contains soda, a double salt is formed containing $\left.\begin{matrix}3K^2O\\Na^2O\end{matrix}\right\}3Nb^2O^5.9H^2O$. By boiling a solution of fluoxyniobate of potassium with acid carbonate of potassium, an acid niobate is obtained, as a pulverulent precipitate containing $K^2O.3Nb^2O^5.5H^2O$.

The *niobates of sodium* are crystalline powders which decompose during washing.

4. *Fluoxyniobates.*—By dissolving niobic acid in hydrofluoric acid, an oxyfluoride of niobium is obtained, having the composition $NbOF^3$, and forming salts isomorphous with the fluotitanates, fluostannates, and fluotungstates.

*Potassium-salts.*—Marignac has obtained five of these salts all perfectly crystallised, namely:

α. $2KF.NbOF^3.H^2O$ crystallising in monoclinic laminæ.
β $3KF.NbOF^3$ „ cuboïd forms (system undetermined).
γ. $3KF.HF.NbOF^3$ „ monoclinic needles.
δ. $5KF.3NbOF^3.H^2O$ „ hexagonal prisms.
ε. $4KF.3NbOF^3.2HO$ „ triclinic prisms.

The first of these is perfectly stable, remaining unchanged after repeated solution and crystallisation, and may therefore be regarded as the normal salt. The others are produced by mixing the solution of this normal salt with neutral or acid fluoride of potassium, or with excess of niobic fluoride; but when either of them is redissolved in hot water, the first crop of crystals deposited from the solution consists of the normal fluoxyniobate. All these salts are completely insoluble in a saturated solution of potassic fluoride.

*Fluoniobate of potassium*, $2KF.NbF^5$, is easily obtained by dissolving the normal fluoxyniobate in hydrofluoric acid, and separates in very brilliant acicular monoclinic crystals. When flused with oxide of lead, it sustains no loss of weight, and is therefore anhydrous.

*Fluoxyniobates of ammonium.*—Marignac has obtained three of these salts, analogous in form and composition to the first, second, and fourth of the potassic fluoxyniobates above mentioned; also a salt crystallising in rectangular prisms, and having the composition $NH^4F.NbOF^3$.

A solution of the lamellar fluoxyniobate in excess of warm hydrofluoric acid, deposits on cooling, groups of short prisms consisting of the salt, $3NH^4F.NbF^5.NbOF^3$.

The *fluoxyniobates of sodium* have not been obtained in definite form, but there appear to be two of them, containing $2NaF.NbOF^3.2H^2O$ and $NaF.NbOF^3.H^2O$.

*Fluoxyniobate of zinc*, $Zn''F^2.NbOF^3.6H^2O$, forms crystals composed of a hexagonal prism and a rhombohedron. The *copper-salt*, $Cu''F^2.NbOF^3.4H^2O$, crystallises in monoclinic prisms.

All these fluoxyniobates, with the exception of one of the potassium- and one of the ammonium-salts, of somewhat complicated constitution, have their corresponding terms, as regards crystalline form and chemical constitution, in the groups of the fluotitanates, fluostannates, fluotungstates, and fluozirconates, the fluorine and oxygen replacing one another isomorphously; thus the acicular potassium-salt, $3KF.HF.NbOF^3$, is isomorphous with fluostannate of potassium, $3KF.HF.SnF^4$; the lamellar ammonium-salt, $2NH^4F.NbOF^3$, with fluotungstate of ammonium, $2NH^4F.WO^2F^2$; the cubic ammonium-salt, $3NH^4F.NbOF^3$, with fluozirconate of ammonium, $3NH^4F.ZrF^4$, &c. It was the isomorphism of these salts which first led Marignac to the discovery of the true constitution of the niobium-compounds.

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END OF THE FOURTH VOLUME.

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# ERRATA IN VOL. IV.

*The asterisk in the second column indicates that the line is to be counted from the bottom.*

| PAGE | LINE | ERROR | CORRECTION |
|---|---|---|---|
| 24 | 26* | $C^{33}H^{30}NO^{2}$ | $C^{33}H^{49}NO^{4}$ |
| 50 | 13 | iii. 997 | iii. 967 |
| — | 18 | 114·8 + 6 . 35·5 | 114·6 + 5 . 35·5 |
| 143 | 17* | from the | from |
| 144 | 7 | $C^{14}H^{11}O^{2}C.^{2}S^{2}O$ | $C^{14}H^{11}O.C^{2}S^{2}O$ |
| 154 | 31 | and hydrocarbonous | and a hydrocarbonous |
| — | 6* | take on the form | take the form |
| 155 | 17 | and variable | and a variable |
| 157 | 30* | , if | , and if |
| 169 | 18 | in these | on these |
| 170 | 20 | or molybdic | *dele* or |
| 171 | 2* | castor-oil, alcohol | castor-oil alcohol |
| 173 | 13* | $C^{6}H^{5}HgS.HgCl$ | *$C^{6}H^{4}HgS.HgCl$* |
| 175 | 3* | heptyl | heptylene |
| 182 | 3* | in | with |
| 184 | 3 | nuts | ante |
| 185 | 31* | [3], 31 | [3], l. 61 |
| 191 | 31* | less | more |
| 192 | 16* | extended | extruded |
| 233 | 30 | $Te(CH^{2})^{2}$ | $Te(CH^{3})^{2}$ |
| — | 41 | $2Te^{iv}\left\{\begin{matrix}(C^{2}H^{5})^{2}\\O''\end{matrix}\right. + 2S^{iv}\left\{\begin{matrix}O''\\(OH)^{2}\end{matrix}\right.$ | $Te^{iv}\left\{\begin{matrix}(C^{2}H^{5})^{2}\\O''\end{matrix}\right. + S^{iv}\left\{\begin{matrix}O'\\(OH)^{2}\end{matrix}\right.$ |
| — | — | $Te^{2}\left\{\begin{matrix}(C^{2}H^{5})^{2}\\(C^{2}H^{5})^{2}\end{matrix}\right. + 2S^{vi}\left\{\begin{matrix}\overset{''}{O}{}^{2}\\(OH)^{2}\end{matrix}\right.$ | $Te''(C^{2}H^{5})^{2} + S^{vi}\left\{\begin{matrix}O''^{2}\\(OH)^{2}\end{matrix}\right.$ |
| 296 | 14* | $H^{2}Cl$ | $HCl$ |
| 317 | 27, 29 and 61 | Logwood | Brazil wood |
| 361 | 35 | Le | Lews |
| 383 | 15 | 0·7 | 0·8 |
| 385 | 28 | as high as | above |
| 398 | 9* | $(NO^{3})^{2}$ | $(NO^{2})^{2}$ |
| 400 | 31* | $H^{4}Ba''$ | $H^{4}Ba''$ |
| 411 | 22 | $\left.\begin{matrix}[C^{12}H^{8}N'''']''\\H^{2}\end{matrix}\right\}\begin{matrix}N\\O^{2}\end{matrix}$ | $\left.\begin{matrix}C^{12}H^{8}(NO^{2})\\H^{2}\end{matrix}\right\}N$ |
| 412 | 22 | diphenylenic | xenylenic |
| — | 25 | phenylenic | xenylenic |
| 418 | 9* | $C^{7}H^{6}O^{2} + C^{6}H^{7}N$ | $C^{7}H^{6}O^{2} + 2C^{6}H^{7}N$ |
| — | — | $C^{7}H^{5}NO + 2H^{2}O$ | $2C^{7}H^{5}NO + H^{2}O$ |
| 425 | 7 | xylyl | formyl |
| 429 | 28 | $H^{2}$ | $H^{2n}$ |
| 430 | 21 | $C^{6}H^{4}N'''$ | $C^{6}H^{3}N'''$ |
| 433 | 3 | 454 | 461 |
| — | 4 | $C^{12}H^{8}N^{2}$ | $C^{12}H^{9}N^{3}$ |
| 436 | 13* | $\left.\begin{matrix}C^{6}HBrN'''\\H\end{matrix}\right\}N^{2}$ | $\left.\begin{matrix}C^{6}HBrN'''\\H\end{matrix}\right\}N$ |
| 443 | 31* | cyaniline | cyananiline |
| 445 | 11 | $2C^{6}H^{7}IN$ | $2C^{6}H^{8}IN$ |

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3 2044 011 218 500

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